

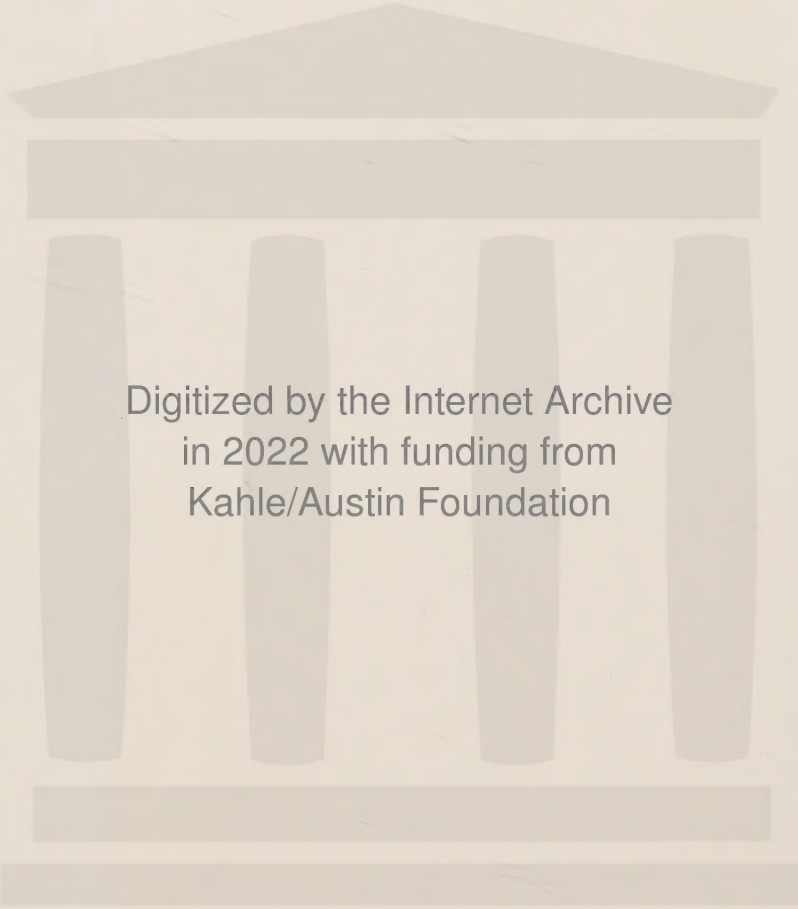
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Electrodics : experimental
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Comprehensive Treatise of Electrochemistry

Volume 9

Electrodeics: Experimental Techniques

COMPREHENSIVE TREATISE OF ELECTROCHEMISTRY

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Comprehensive Treatise of Electrochemistry

Volume 9

Electrodics: Experimental Techniques

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This volume of the Comprehensive Treatise of Electrochemistry is dedicated to the memory of

Professor I. EPELBOIN

who was the director of the CNRS Laboratory for the Physics of Liquids and Electrochemistry at the University of Paris, and

Professor CHARLES REILLEY

who was Professor of Chemistry at the University of North Carolina. Both of these distinguished electrochemists coauthored chapters in this volume and passed away shortly thereafter, before this volume went to press. Both made a number of very important contributions to various areas of electrochemistry. Their contributions to those aspects of electrochemistry involving methodology are well reflected by their chapters in this Treatise.

The Editors

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Preface to Comprehensive Treatise of Electrochemistry

Electrochemistry is one of the oldest defined areas in physical science, and there was a time, less than 50 years ago, when one saw "Institute of Electrochemistry and Physical Chemistry" in the chemistry buildings of European universities. But after early brilliant developments in electrode processes at the beginning of the twentieth century and in solution chemistry during the 1930s, electrochemistry fell into a period of decline which lasted for several decades. Electrochemical systems were too complex for the theoretical concepts of the quantum theory. They were too little understood at a phenomenological level to allow the ubiquity in application in so many fields to be comprehended.

However, a new growth began faintly in the late 1940s, and clearly in the 1950s. This growth was exemplified by the formation in 1949 of what is now called The International Society for Electrochemistry. The usefulness of electrochemistry as a basis for understanding conservation was the focal point in the founding of this Society. Another very important event was the choice by NASA in 1958 of fuel cells to provide the auxiliary power for space vehicles.

With the new era of diminishing usefulness of the fossil fuels upon us, the role of electrochemical technology is widened (energy storage, conversion, enhanced attention to conservation, direct use of electricity from nuclear-solar plants, finding materials which interface well with hydrogen). This strong new interest is not only in the technological applications of electrochemistry. Quantum chemists have taken an interest in redox processes. Organic chemists are interested in situations where the energy of electrons is as easily controlled as it is at electrodes. Some biological processes are now seen in electrodic terms, with electron transfer to and from materials which would earlier have been considered to be insulators.

It is now time for a comprehensive treatise to look at the whole field of electrochemistry.

The present treatise was conceived in 1974, and the earliest invitations to authors for contributions were made in 1975. The completion of the early volumes has been delayed by various factors.

There has been no attempt to make each article emphasize the most recent situation at the expense of an overall statement of the modern view. This treatise is not a collection of articles from *Recent Advances in Electrochemistry* or *Modern Aspects of Electrochemistry*. It is an attempt at making a mature statement about the present position in the vast area of what is best looked at as a new interdisciplinary field.

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Preface to Volume 9

This volume covers the more traditional electrochemical methods for the study of electrochemical interfaces and the kinetics of processes occurring at such interfaces. Chapter 1 presents an introduction and overview of steady state and non-steady state techniques. Chapter 2 on solutions, cells, and surfaces is of special importance since the experimental studies of electrode kinetics have been often severely impeded by the use of cells with mass transport and current distribution problems, impure solutions, and nonreproducible, non-well-defined electrode surfaces. The third and fourth chapters focus on the non-steady state and ac techniques with substantial interaction between the authors of the two chapters during their preparation. Chapters 5 and 6 are concerned with two types of electrode-cell configuration which have proved particularly important in fundamental studies of adsorption and kinetics: the rotating disk and ring disk electrodes and the thin layer cell technique. The final chapter, Chapter 7, is concerned with the radio tracer techniques which are particularly important for the study of adsorption on electrodes.

The reader is referred to Volume 8 of this Treatise for a discussion of both the *in-situ* and *ex-situ* spectroscopic techniques as applied to the study of electrode systems. The combined use of advanced electrochemical methods and *in-situ* spectroscopic techniques offers great promise for furthering the understanding of electrochemical interfaces and processes occurring thereat on a molecular level.

Case Western Reserve University
Texas A&M University
University of Ottawa
Giner, Inc.

Ernest B. Yeager
John O'M. Bockris
Brian E. Conway
S. Sarangapani

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1

Overview of Electrochemical Methods for the Study of Electrode Kinetics

S. SARANGAPANI and ERNEST YEAGER

1. Introduction

1.1. Steady State and Transient Methods

The technique for characterizing the kinetics of electrode reactions can be divided into steady state and transient methods. The former involves the evaluation of the current potential relations with either the potential (potentiostatic control) or the current (galvanostatic control) held at constant values for sufficient times that the other quantity approaches an essentially constant value. The nonsteady state methods involve the perturbation of the system from either equilibrium or a steady state condition and the following of the response of the system as a function of time using current, potential, charge, impedance, or any other accessible property of the interface to follow the response. The relaxation methods are a subclass of the perturbation methods and involve the perturbation of the system from equilibrium with the relaxation of the system *back to equilibrium* followed by any convenient parameter indicative of the state of the electrochemical system (e.g., charge, potential, optical reflectance). Usually the perturbation involved in the relaxation

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approach is sufficiently small that the system is in the linear response range, i.e., the rate of restoration or return to equilibrium is directly proportional to the displacement from equilibrium. This facilitates the development of analytical equations relating the relaxation times[†] to the exchange current density, the electrode capacitance, and mass transport parameters.

1.2. Thermodynamics

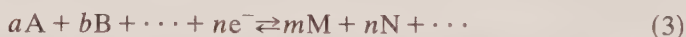
Kinetic studies presuppose a knowledge of the thermodynamics of the system. A study of electrode potential as a function of the system variables (temperature, pressure, concentration) will yield the necessary thermodynamic information, provided the system is reversible on open circuit. Thermodynamic data can also be calculated using free energies of formation and partial molal properties of the system components. This approach is especially suitable for irreversible systems for which experimental determination of the reversible potential may pose difficulties. Further details of these methods are given by MacInnes⁽¹⁾ and Latimer.⁽²⁾

1.3. Parameters To Be Measured in Kinetic Studies

The basic kinetic parameters needed to characterize an electrode reaction are:

- (1) Reaction orders (ν_i)
- (2) Standard rate constants (k°)
- (3) symmetry factors for the rate-controlling step (β)
- (4) Stoichiometric coefficient (ν)
- (5) Standard heats and entropies of activation ($\Delta H_0^\ddagger$ and $\Delta S_0^\ddagger$)

The involvement of these parameters in electrode kinetics is evident from the following generalized equation for an overall electrochemical reaction of the form:



Under the assumption that specific adsorption of reactants and products is absent and that there are no complications due to the ionic double layer and

[†] For small displacement from equilibrium, the rate of return to equilibrium is related to the displacement from equilibrium by an equation of the form:

$$\frac{d\Delta X}{dt} = -(1/\tau)X \quad (1)$$

When X is a parameter indicating the small displacement from equilibrium and τ is the relaxation time. Integration of Eq. 1 yields

$$\Delta X = A \exp(-t/\tau) \quad (2)$$

where a is the displacement at time $t = 0$.

mass transfer, we have for the rate laws:

$$I_a = \left(\frac{n}{\nu}\right) F A k_a \prod_i c_i^{\nu_{i,a}} \quad (4)$$

and

$$I_c = \left(\frac{n}{\nu}\right) F A k_c \prod_i c_i^{\nu_{i,c}} \quad (5)$$

with $I = I_a - I_c$, where the subscripts c and a denote the cathodic and anodic partial reactions, k_a and k_c are the rate constants and generally are functions of the electrode potential, A is the electrode area, and F is the Faraday. The quantity I/nF would then yield the net rate. Consideration of specific adsorption or chemisorption involves the replacement of concentration c_i with terms which are functions of the surface coverage. This is done through the use of an appropriate adsorption isotherm. When the coverage is not low (i.e., not in the Langmuir range), this may lead to the need for considerably more complex rate equations, as have been given by Despic.⁽³⁾ The influence of mass transfer can be treated by replacing the bulk concentration terms with the concentration at the electrode surface. Since the current depends on the surface concentration, a quantitative treatment of mass transfer process is necessary to arrive at the exact relationships. For details, see Vol. 6 of this treatise.

In Eqs. (4) and (5), n is the charge number of the reaction as written [see Eq. (3)] and ν_i is the order of the reaction with respect to the reactant denoted by the subscript. This latter quantity need not be integral and may assume positive or negative values. The term ν is the stoichiometric number and is the number of times the rate-determining step occurs for the completion of the overall reaction [Eq. (3)] as formulated; ν is always a positive number.

The rate constant of an electrode reaction as written in Eqs. (4) and (5) is a potential-dependent parameter and has the form:

$$k_c = k^\circ \exp[-(\alpha_c n F / \nu R T)(E - E^\circ)] \quad (6)$$

$$k_a = k^\circ \exp[(\alpha_a n F / \nu R T)(E - E^\circ)] \quad (7)$$

where k° is the rate constant corresponding to the standard potential E° .

In the discussion above, we have not taken into account the influence of double layer structure. Because of the presence of the double layer, the surface concentration is not the same as the bulk concentration. The potential drop across the diffuse layer also modifies the portion of the applied potential which influences the rate constants in Eqs. (6) and (7). For a simple first-order rate step (e.g., a redox type reaction) not involving specific ionic adsorption, application of the Frumkin correction to the rate constant yields⁽⁴⁾

$$k^\circ = k^{\circ'} \exp \left[\frac{(\alpha n - z) F \phi_2}{R T} \right] \quad (8)$$

where ϕ_2 is the potential drop across the diffuse ionic layer and z is the charge of the reactant. With more complex reactions involving adsorbed reactants, products, and/or intermediates, the corrections for double layer effects become very complex and difficult to apply.

To minimize ionic double layer effects a high concentration of a supporting electrolyte is often used in electrode kinetic studies, thus reducing the potential drop ϕ_2 across the diffuse ionic layer. The supporting electrolyte should not be specifically adsorbed over the potential range of the kinetic studies. The electrolyte most frequently used for this purpose is NaF. When the charge of any of the reactants is greater than unity, however, the double layer corrections are significant even with supporting electrolyte concentrations of 1 M.

Equation (8) still only represents the equilibrium double layer situation and for this reason is known as the "Frumkin static correction." During the investigation of fast processes, nonequilibrium situations can arise in the ionic double layer as the thickness of the mass transport diffusion layer approaches that of the diffuse layer of the ionic double layer. The cross interaction of mass transport and the ionic double layer has been treated by various researchers including Levich,⁽⁵⁾ Matsuda and Delahay,⁽⁶⁾ Rangarajan,^(7,8) and Budevski.⁽⁹⁾

The term α used in the kinetic equations above is known as the apparent transfer coefficient and generally is a complex quantity. It is related to the symmetry factor (β) and the number of electrons involved in the rate-determining step (rds). For an overall reaction involving both electrochemical and chemical steps⁽⁶⁾

$$\alpha_c = (n'/\nu) + n''\beta \quad (9)$$

$$\alpha_a = (n - n'/\nu) - n''\beta \quad (10)$$

$$\alpha_c + \alpha_a = n/\nu \quad (11)$$

where n' = number of electrons transferred before the rds; n'' = the number transferred during the rds; n = total number of electrons transferred. When the reactants, products, and/or intermediates are specifically adsorbed and the coverage is substantial (e.g., $\Theta > 0.2$), Eqs. (9) and (10) are no longer applicable and a much more complex relationship exists. Despic⁽³⁾ has treated this situation in terms of Temkin type adsorption and kinetics.

Equation (12) shows that $\alpha_a + \alpha_c$ need not be equal to 1. For purely electron transfer reactions, Devanathan⁽¹¹⁾ has given tables of α for 2, 3, 4, and n electron transfer reactions. Discussion of the α problem can also be found in both references 10 and 11.

The terms α_c and α_a can be determined using the Tafel slopes:

$$1/b_c = -\alpha_c F/RT = (\partial \ln I_c / \partial E) \quad (12)$$

$$1/b_a = \alpha_a F/RT = (\partial \ln I_a / \partial E) \quad (13)$$

where b_c and b_a are the cathodic and anodic Tafel slopes, respectively.

The small perturbation-relaxation methods are in the linear response range and hence do not yield the Tafel slopes or apparent transfer coefficients directly. These methods do yield the exchange current. The terms α_c and α_a can be determined from the dependence of the exchange current on reactant and product concentrations. For a simple one-step, one-electron redox type reaction which is first order in the cathodic and anodic directions, the exchange current is given by

$$I_0 = AFk^\circ C_c^{\alpha_a} C_a^{\alpha_c} \quad (14)$$

When a multistep reaction is involved with adsorption of reactants and/or products, the corresponding equations for the exchange current may become more complex.⁽³⁾

The stoichiometric number ν represents the number of times the rds occurs for the completion of the overall reaction *as written*. An overall reaction can be written in more than one way, e.g., $2\text{H}^+ + 2\text{e} \rightarrow \text{H}_2$ or $\text{H}^+ + \text{e} \rightarrow 1/2\text{H}_2$. This ambiguity can be removed by considering the ratio n/ν , which is indicative of the true characteristic of the electrode reaction. The n/ν ratio can be obtained from the anodic and cathodic Tafel slopes (b_a , b_c) since according to Eqs. (12–13)

$$\frac{n}{\nu} = \frac{RT}{F} \left(\frac{1}{b_a} - \frac{1}{b_c} \right) \quad (15)$$

For Eq. (15) to be valid, however, requires that the mechanism, the rate-determining step, and the standard rate constants be the same for both the anodic and cathodic branches. Equation (16) is followed by simple systems such as the redox couples and also relatively reversible catalytic processes such as hydrogen generation and oxidation on platinum and the oxygen-hydrogen peroxide couple. For more irreversible catalytic processes, when the anodic and cathodic Tafel regions are widely separated in potential (e.g., the $\text{O}_2/\text{H}_2\text{O}$ reaction), the anodic and cathodic surface conditions are quite different and Eq. (15) is usually not applicable. It may still be possible to obtain ν/n from the charge transfer resistance $R_{ct} = dE/dI$, measured near the reversible potential using the equation

$$R_{ct} = (\nu/n)(RT/F) \cdot (I/I_0) \quad (16)$$

with I_0 evaluated from either the anodic or cathodic Tafel regions or better yet by fitting the experimental overpotential data to the complete kinetic equation over a potential range including the reversible potential, but sufficient for the nonlinear terms to be significant.

The true heat and entropy of activation cannot be determined for an electrochemical reaction without questionable assumptions. Only the values at a constant overpotential relative to the reversible potential of the electrode reaction are accessible. The relative values are obtained from the temperature dependence of the rate constant. The reader is referred to the literature for

a discussion of the extraction of the apparent heat of activation from the experimental temperature dependence of the kinetics and the use of such data in examining various mechanisms.^(12,13)

The details of determination of kinetic parameters and proofs of alternative mechanisms for hydrogen evolution and oxygen reduction reactions are discussed in Chapters 5 and 6 of Volume 7 of this series. The reader should bear in mind that kinetic data rarely, if ever, prove a mechanism, but can be a powerful tool for verifying various proposed mechanisms.

2. General Aspects of Electrochemical Methods

Steady state techniques are those class of experiments in which a direct current or potential of a given amplitude is applied to the system and the steady state response is observed. Methods employing an alternating potential may also be considered steady state. While the system is not in its steady state in its instantaneous response, within any one cycle, the ac current-voltage response or the impedance averaged over a cycle is the steady state value. Nonsteady state techniques are those methods in which the system is perturbed by a signal and its relaxation to equilibrium or another stationary state is observed as a function of time. There are circumstances under which one may prefer one or the other of these methods. The following discussion cites a few of the general features, advantages, and disadvantages of these two classes of methods.

Any change in the electrical state of an electrochemical system results in the rearrangement of charges at the electrical double layer. The resulting displacement current density can be expressed by

$$i_{dl} = \frac{\partial q}{\partial t} = \frac{\partial}{\partial t} \int_{E_z}^E C dE \quad (17)$$

where q = charge per unit area, C = differential capacity/unit area, E_z = potential of zero charge, and i_{dl} = current required to charge the double layer. For small amplitude perturbations, Eq. (17) can be replaced by

$$i_{dl} = C(dE/dt) \quad (18)$$

provided the potential dependence of the capacitance is not very steep. For steady state techniques $dE/dt = 0$, and hence $i_{dl} = 0$, i.e., no double layer charging correction is necessary. Since the capacitance data are not obtained with the steady state nonrelaxational methods, however, the adsorption information is lost.

For nonsteady state measurements, this double layer charging correction usually becomes important. A complication arises in attempting to make this correction, especially in the case of fast reactions. Randles⁽¹⁴⁾ assumed that the double layer can be represented by a simple capacitance whose value would not be affected by the presence of a faradaic process or the reactants

participating in such a process in the presence of a large concentration of a supporting electrolyte. The nonfaradaic capacitance associated with the double layer was then obtained from the impedance data with only the supporting electrolyte present and the value then used to correct the data with the species involved in the faradaic process added. The assumption that these latter species do not influence the double layer capacitance is often questionable. Sluyters *et al.*⁽¹⁵⁾ have avoided this assumption by developing a method of analysis for a.c. impedance data, which allows the double layer capacitance to be determined and accounted for with the reacting species present. Delahay⁽¹⁶⁾ showed that the *a priori* separation of faradaic and nonfaradaic capacitance is impossible through a detailed consideration of the fluxes of the electroactive components, the total current, and the surface excesses of various charged components. Barker,⁽¹⁷⁾ as well as Sluyters *et al.*,⁽¹⁵⁾ has questioned the practical importance of the various terms in Delahay's equations. It appears that, for most reactions, satisfactory double layer correction can be carried out provided the effects of all electrolyte components on the double layer capacitance are taken into account. A detailed account of this problem is available in Section 5.4 of Chapter 4 of this volume.

Both steady state and nonsteady state methods usually require mass transport correction for an accurate evaluation of the rate parameters. With the steady state methods, the steady state is approached when the system is under forced or natural convection and the concentration profile at the surface has achieved a time invariance. The correction of the current-voltage data for mass transport to extract the kinetic parameters is relatively simple for situations when the Nernst diffusion layer is uniform across the electrode surface, as is the situation with the rotating disk electrode configuration. (See Chapter 5 of this volume.)

With most of the nonsteady state techniques, the systems are examined in the absence of forced convection with the observation times too short for natural convection to be established. The treatments take into account the time dependence of the concentration gradients in reactants and products in the electrolyte phase and in some instances the electrode phase. This leads to some complex expressions for the nonsteady state methods. For small amplitude perturbations, analytical solutions of the differential equations taking into account transport are generally available for all the common perturbation methods. For large amplitude perturbations, computer simulation techniques are usually quite adequate (see, e.g., Feldberg⁽¹⁸⁾) and permit extraction of the kinetic parameters. In some instances, the potential dependence of the double layer capacitance must be considered.

With both the steady state and nonsteady state techniques, the electrode configuration should be such as to ensure reasonably uniform current distribution. Nonuniform current distribution can severely complicate the extraction of relative rate constants from experimental data, particularly when the kinetics are not first order in the reactants and/or products.

Table 1
Typical Electrochemical Methods for the Study of Electrode Kinetics

Method	Input	Response	Max. (k_0) (cm/s)	Remarks	Reference
Steady state					
1. Direct potentiostatic			10^{-2}	Instrumentation simple. Progressive changes in electrode surface cause serious problems with solid electrodes. Can be carried out with very slow voltage sweep (sufficiently slow for capacitive current to be negligible).	20, 21
2. Direct galvanostatic			10^{-2}	Instrumentation very simple. Progressive changes in electrode surface cause serious problems with solid electrodes. Can be carried out with ramp function of low slope. Not recommended for systems involving limiting currents or maxima in i versus E curves.	20, 21
3. Indirect galvanostatic			10^{-2}	Yields steady state polarization, but also can be used to obtain E versus t information after interruption of current. The initial slope S of the E - t response corresponds to the capacitive component of the interphase. Virtually eliminates IR correction problem without use of Luggin capillary when current distribution is uniform. (Other remarks same as for direct galvanostatic method.)	19, 22

Reference to
this volumeNonsteady state
4. Single potential step 10^0

IR drop between working and reference electrodes must be very small. Requires correction at short times for double layer charging. Requires fast action potentiostat plus oscilloscope or digital transient storage system.

5. Double potential step

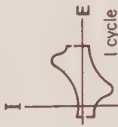
 10^0

Faradaic and nonfaradaic capacitive components relatively easily separated.

Offers advantages for study of short-lived reaction intermediates. Simplification of theory for CE reactions can be obtained by measuring the charge rather than the current. Very useful in the study of electrocrystallization.

Chapter 3,
4.2.1.26. Rectangular potential
function 10^0

Mathematical treatment complex unless upper and lower potentials carefully chosen. May offer promise for the study of parallel electrode reactions and also reactions with unstable intermediates. Has not found wide application.

Chapter 3,
4.2.1.37. Cyclic linear
sweep voltammetry 10^{-1}

Complete theoretical analysis complex. Yields information concerning adsorption kinetics (particularly fast). Effective technique for preliminary examination of surface. *IR* drop between working and reference electrodes must be very small. Requires fast action potentiostat plus digital storage oscilloscope for fast sweeps. Reversibility of redox couples can be checked, electroactive intermediates can be detected, presence of multiple steps in a reaction mechanism may be discerned. Semi-integral or convolutive procedures useful in *IR*, establishing concentration of reactants at electrode surface at any point in cyclic voltammetric curves.

Chapter 3,
4.1

Table 1 (continued)

Method	Input	Response	Max. (k_0) (cm/s)	Remarks	Reference
8. Single current step			10^0	Instrumentation relatively simple (pulsed galvanostat plus digital storage oscilloscope). Relatively easy to correct for IR drop. Requires correction for double layer charging.	Chapter 3, 4.2.1.1
9. Double current step			10^4	Adjust height-width of first current pulse such that $(dE/dt) = 0$ at beginning of second current pulse. Avoids double layer contribution to faradaic current. Requires more complex instrumentation than single current step method (double current pulse generator plus oscilloscope). Relatively easy to correct for IR drop. For very fast kinetics, must consider diffuse layer-diffusion layer interactions.	Chapter 3, 4.2.2.3.2
10. Exponential current pulse			10^0	An input of exponentially decaying current $i = \Delta i \exp(-t/\tau)$ is applied. The response has a maximum. Instrumentation is simple. Activation/diffusion effects can be studied. If activation overpotential (η) alone is important (sufficiently low times), $\eta_{\max}$ vs. $t_{\max}$ can provide i_0 directly. A study of $d\eta/dr$ at $r^{1/2} = 0.954$ eliminates diffusional contributions.	Chapter 3, 4.3

Table 1 (continued)

Method	Input	Response	Max. (k_0) (cm/s)	Remarks	Reference
16. Pressure step techniques			10^0	After disturbance, relaxation is similar to that with electrical perturbation techniques. Offers advantage that fast kinetics can be studied in systems with insufficient conductivity to pass appreciable current. Pressure step easily obtained with bursting diaphragm (10^{-5} s resolution).	Chapter 3, 5.2
17. Concentration perturbation			10^{-1}	After disturbance, relaxation is similar to that with electrical perturbation techniques. Offers advantage that high resistivity can be tolerated. Flow techniques provide convenient means for producing change in bulk concentration (10^{-3} s resolution).	Chapter 3, 5.4

Steady state methods provide data of applied significance even when the mechanism is not fully understood. The steady state current-voltage data under well-defined conditions are necessary for the design and optimization of electrochemical cells for various applications.

The upper limit for the rate constants that can be determined by a steady state method is set by mass transport conditions. For a first order process, this upper limit for the standard rate constant is of the order of $\sim 10^{-2}$ cm/s with a method such as the rotating disk electrode technique which permits the Nernst diffusion layer thickness to be depressed to $\sim 3 \times 10^{-4}$ cm. Nonsteady state methods can be used to determine standard first-order rate constants as high as 10 cm/s. They may also be less susceptible to impurity effects due to the short duration of the experiment and the absence of convection. Nonsteady state methods do not require the long-term stability of the electrode surface necessary for steady state methods and hence are applicable to electrode systems with changing surfaces such as corroding metals.

Some of the more common electrochemical methods are listed in Table 1 together with the upper limit for the first-order rate constants which can be determined with each method using modern instrumentation and retaining an accuracy of $\sim 10\%$. Some comments concerning the methods are also included together with a reference, either a chapter in this volume or another readily available reference. The table is a revision of an earlier table [from Reference 19].

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2

Surfaces, Cells, and Solutions for Kinetics Studies

H. ANGERSTEIN-KOZLOWSKA

1. The Components of an Electrochemical System

In an experimental set-up for electrode-kinetic studies, several independent components have to be considered. The electrodes and the electrolyte form the primary components of an electrochemical system, in which the electrochemical reaction to be studied takes place. Normally, the process of interest occurs at the interface of the working electrode and the electrolyte, except in special cases, e.g., ion transfer across fluid interfaces. The next component is the electrochemical cell—the container in which the system studied is to be enclosed. The final components are the substances which may enter the system during measurements, usually gases bubbled through the solution or reagents added. It is most important that all the components used be rigorously purified or cleaned, and do not react chemically with each other, and that no impurities should enter the system during measurements, so that the system will not contain any other constituents than those intended.

The necessity for ultra-pure conditions in electrode-kinetic and electroabsorption studies was recognized first by Frumkin⁽¹⁾ and other Russian workers in the thirties, and in the West by Bockris and Conway⁽²⁾ in the fifties and Schuldiner⁽³⁾ in the sixties. These guidelines for electrode preparation and cleaning, and for cleaning of glassware, water, and chemicals for the supporting

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electrolyte and reagents have been followed by electrochemists for nearly a quarter of a century. At that time, the standard procedure for water purification was double distillation, the second time being with an oxidizing agent, usually alkaline permanganate solution in an all-quartz apparatus. This usually gave satisfactory results, and a final purification of the solution by *in situ* pre-electrolysis was sufficient to obtain the necessary degree of cleanliness, assuring reproducible experimental results.⁽²⁾ Although Schuldiner⁽³⁾ a long time ago directed attention to the desirability of conducting specially sensitive electrochemical work in controlled-atmosphere rooms, this has not become a common practice.

Nowadays, nitrogen "tents," plastic bags, or airtight glove boxes with purified nitrogen passing through are used not only for nonaqueous electrochemical measurements to protect the systems from contamination by atmospheric moisture, but are recommended⁽⁴⁾ also for electrochemical surface studies in aqueous solutions in order to protect the solutions from contamination by city air or CO₂.

Although the purity of chemicals and of metals used for electrodes has greatly improved, and new chemically inert materials for cell construction are available, nevertheless the deterioration of the environment, the pollution of city air and especially the presence of organic surface-active, steam-volatile species in waters has introduced new difficulties in achieving the cleanliness needed for satisfactory electrode-kinetic and electrosorption studies.

The common sources of impurities in an electrochemical system are listed in Table 1. Impurities can (i) be introduced by the system components themselves, mainly through chemicals and solvents which, after conventional purification, may still contain electrochemically significant traces of some impurities and/or (ii) appear during the course of the measurements. The success or failure of an experimental piece of work may quite often depend on the extent to which the system under investigation can be maintained in a closed state, i.e., without any contaminants from outside interfering.

The proper choice, design, preparation, and cleaning of the components of electrochemical systems will be the topic of this chapter.

2. Electrodes

Modern studies on electrosorption and electrocatalysis, coupled with the results of recent research in the field of "high-vacuum" surface science, have led to the realization of the paramount importance of clean electrode surfaces for obtaining meaningful and reproducible results in electrode-kinetic studies, especially in those reactions where an intermediate of the reaction is formed in a chemisorbed state on the electrode. Hence the condition of electrode surfaces requires careful attention, so that proper and reproducible cleaning procedures are required, as will be described below.

Table 1
Sources of Impurities in an Electrochemical System

Components	Impurities	
	Present initially	Appearing in time due to
1. Electrodes	—	Leaking or faulty seal
2. Electrolyte		
a) solute	+	Decomposition by chemical or electrochemical reactions
b) solvent	+	
3. Cell	—	Diffusion from ground-glass joint; wrong design of the cell; desorption from cell walls; leaching of cell materials.
4. Gases		Inefficient cleaning of gas line; desorption from old charcoal traps in gas line.
5. Lab air		Diffusion through ground-glass joints or other fittings which are not airtight.

2.1. Preparation and Cleaning of Solid Electrodes

The electrode material for any electrode-kinetic or interfacial study should be of the highest purity available, preferably the 99.999% or “spectroscopically pure” grade, so that no further purification is required. Then preparation of a suitable electrode involves only: (i) cleaning of the electrode surface from impurities collected on it during the manufacturing or handling processes; (ii) proper mounting of the metal; (iii) cleaning from any impurities acquired during the mounting process; and (iv), for the working electrode, final standardizing of the surface *in situ* before the run. The individual steps involved in preparation of electrodes will now be discussed in detail.

2.1.1. Degreasing

The electrode material for solid electrodes, usually supplied in the form of cold-drawn wires or gauzes, cold-rolled sheets, or nowadays more and more frequently in the form of monocrystals, is nearly always contaminated on its surface with impurities originating from the drawing or rolling procedures, or acquired during handling and storage. Removal of these impurities should always be the first cleaning procedure. This is best done by degreasing with acetone under reflux in a Soxhlet type apparatus for 12 to 24 h. Afterwards the metal should only be touched by clean platinum-tipped tweezers or through filter paper.

2.1.2. Annealing

To obtain reproducible results, when not only the surface, but also the bulk of the electrode material will take part in an electrochemical reaction, e.g., as in the case of hydrogen absorption into Pd or Fe, hydrogen diffusion, or multilayer oxide formation, any stress in the metal from cold-working has to be removed by annealing the electrode material under vacuum at an appropriate temperature for one half to one hour followed by slow cooling to room temperature. Some annealing temperatures, which have been used in electrochemical work with good results, are given in Table 2. Normally the annealing temperatures are related to the Tammann temperature of the metal concerned.

When removal of a surface oxide is essential, and possible by annealing, it should be done first in a stream of purified hydrogen, then in vacuum. Vacuum rather than a nitrogen atmosphere should be used, since nitrogen, for many metals, does not behave as an inert gas at high temperatures, or with some metals, e.g., Li, even at ordinary temperatures. It should be stressed that no annealing should be undertaken unless organic impurities have first been removed from the surface by the degreasing procedure mentioned above; otherwise cracking of the organic material will result in carbon residues being "baked" into the surface, making subsequent cleaning very difficult, if not impossible.

2.1.3. Mounting of Electrode Metals

Electrode materials degreased, or degreased and annealed, in one of the ways mentioned above, can now be mounted. Wires of metals such as Pt, Pd, or Au, which can be heated in a flame, can be successfully sealed into soft glass tubes or capillaries, carefully precleaned from outside *and inside*. Although the inside of the tube will not be in contact with the solution, any impurities present on the inside surface will impede the wetting of the metal by the glass and the resulting seal will not be leakproof. Also some of these impurities may collect on the surface of the metal material during the sealing operation.

Table 2
*Annealing Temperatures for Some
Metal Electrodes*

Metal	Temperature, °C
Pt	900
Au	550
Ni	600
Fe	900

During the electrode sealing procedure, special care should be taken to avoid the creation of any potential gas pockets, or capillary openings which cannot, practically, be cleaned, and from which any impurities present will subsequently slowly diffuse into the solution adjacent to the electrode surface (Figure 1a). A proper seal, as shown in Figure 1b, will result, when after the seal is made, but just before the glass has become hard, the wire is gently pulled out. An alternative solution would be an electrode construction, which avoids the electrolyte contact with the Pt-glass seal as described by Visscher,⁽⁵⁾ who reported the very characteristic distortions of potentiodynamic i - E profiles which can arise on account of oxygen diffusion from minute cracks in the glass seal. It is of interest to recall that the thin layer cell procedures of Christensen and Anson⁽⁶⁾ originated from the unusual behavior of a redox system at an electrode having a cracked seal.

Wires of Pt and Au can also be sealed in Pyrex glass tubes despite the difference in expansion coefficients. However, due to the stress which develops in the glass, the life of the seal will be limited. Electrodes in the form of sheets or gauzes are usually spot-welded to short wires sealed in glass. A wire flattened in the region where the seal is to be made gives a more durable seal in Pyrex glass.

Special precautions have to be taken when a contact of the hot metal with air or combustion gases has to be avoided. A procedure for electrode sealing developed by Bockris and Conway^(7,8) in the fifties is simple and gives exceptionally reproducible surfaces. It involves heating electrode wires in glass



Figure 1. Electrode mounting: (a) an incorrect type of seal; (b) a proper seal.

tubes in purified hydrogen and sealing the electrodes in a hydrogen atmosphere in thin glass bulbs connected to the tubes. The bulbs are then mounted in the cell and subsequently broken under the solution with an appropriate potential applied. This procedure was later modified by sealing the tubes with the thin glass bulbs to a small quartz oven, so that not only the atmosphere, but also the annealing temperature could be controlled. An extension of the procedure was described by Conway⁽⁹⁾ for preparation of Pb electrodes by melting in H₂ and sealing a Pb-drop electrode in a glass bulb.

Electrodes sealed in the thin bulbs are well suited for steady-state measurements. For fast transient experiments, however, for which small electrodes are used in order to avoid high currents, serious complications can arise due to the shielding effect by the umbrella-like remaining parts of the broken bulb.⁽⁸⁾ For such methods, straightforward sealing is to be preferred. According to the author's experience, no difference can be observed in the electrochemical behavior of Pt and Au electrodes sealed and annealed in glass bulbs or cleaned without annealing, although Gilroy and Conway⁽¹⁰⁾ found that better reproducibility is obtained with smooth Pt electrodes heated and sealed in hydrogen than those sealed and treated in a flame.

Sealing electrodes into glass bulbs is also very useful when purification of the solution by pre-electrolysis is desired; then the electrodes in their protective glass envelopes can be maintained in the cell and solution while pre-electrolysis proceeds without being contaminated by the incompletely purified electrolyte solution or becoming corroded, depending on the properties of the metal.

Electrodes which become oxidized when heated in air, or for which no glass can be found with a similar expansion coefficient, are best mounted in shrinkable Teflon tubes or Kel-F; both these materials have been found to be satisfactorily inert in acid and alkaline electrolytes. As in the case of glass seals, care must be taken not to leave any capillary or annular opening between the electrode and the Teflon tube.

When the electrode is in the form of a sheet, or has an irregular shape, which excludes mounting in Teflon, the electrode is often spot-welded to, or hung on, a Pt hook sealed in glass. However, the possibility of local cell corrosions has first to be excluded before two different materials in contact with each other are put in a solution. Even without the possibility of corrosion, precautions should be taken to cover the wire hook carefully with the electrode material by plating or to keep the wire above the solution level, as serious errors in the significance or interpretation of results can arise from currents which can pass on the small Pt wire, especially if the reaction overvoltage on it is lower than on the main electrode material. Also, if potentiodynamic sweeps are made, a surface process may occur on the wire support and give rise, at high sweep rates, to currents competing, e.g., with a diffusion-controlled current for the process under examination at the large electrode to be investigated.

Sealing electrodes into glass tubes by means of an epoxy resin will produce good results only if the electrode material can be etched or electropolished afterwards to remove components of the hardener which become adsorbed on, or migrate to, the metal surface. Such adsorbed impurities can also be removed by prolonged washing with pyridine but, as was found by Sharp,⁽¹¹⁾ the resolution of the 4 ~ 5 states of chemisorbed H on Pt wires mounted in epoxy resin was never quite as good as with electrodes sealed in soft glass or mounted in Teflon. The epoxy seal is resistant to dilute acid solutions but not to concentrated H_2SO_4 , so that the final cleaning after mounting poses some problems if this method of sealing is adopted. This method is more suitable for electroplating or corrosion studies with base metals that cannot be sealed in glass.

2.1.4. Final Cleaning

Electrodes sealed in glass or shrinkable Teflon are finally cleaned overnight in, e.g., concentrated H_2SO_4 , in the case of noble metals, rinsed in pyrodistilled water (see below), then with the ultra-pure solution and placed, still wet, in the cell solution. Pt electrodes prepared in this way can show already on the second or third potentiodynamic sweep the proper well-resolved i - E profile which does not change with further sweeping.⁽¹²⁾

Many much more elaborate cleaning procedures have been reported in the literature, including polishing of the surface with emery paper, abrasion, soaking in organic solvents or chromic acid, even in aqua regia, storing for long periods in distilled water before use, etc. All these drastic methods are really not necessary in most cases. On the contrary, they can often contaminate the surface: for example, chromic acid treatment can produce a surface irrevocably contaminated with chromium, or soaking in not freshly distilled ether or acetone can bring irreversibly adsorbed organic impurities onto the surface rather than remove them. Abrasion of metals, often used in older works, can only contaminate the metal chemically or physically with included particles and often produces crystallographically disturbed Beilby layers. If the starting materials are of high-purity grade, only substances adsorbed on the metal, not layers of the metal itself, have to be removed to produce a clean surface. All the measures, which in a drastic way attack the surface, e.g., abrasion, use of strong oxidizing acids, yield solid electrodes with poorly defined and usually nonreproducible surfaces. These methods should only be used in special cases, e.g., when a layer formed from some previous reaction has to be removed mechanically for re-use of an electrode or when polished surfaces for optical or electro-optical measurements are required.

All electrodes which will be in contact with a test solution should be cleaned as described above.

2.2. Working Electrodes

2.2.1. Pre-treatment

The necessity for standardizing the working electrode surface immediately prior to experimental measurements has been well appreciated for a long time. The pre-treatment has to be adjusted to the type of studies involved and to the electrode metal used. Usually, for noble metals, it consists of an electrochemical program of potential steps or potential sweeps which, e.g., by oxidizing and reducing the surface, cleans it finally from oxide and minute traces of adsorbable impurities acquired from air during the cell assembly procedure and brings the electrode always to a reproducible surface state at the reaction potential. The pre-treatment is followed by a potential program appropriate for the desired experimental measurements. It has to be stressed that the aim of this kind of pre-treatment should be to standardize the electrode surface, not to clean it extensively or purify the solution.

2.2.2. Polishing of Surfaces

Polishing of electrode surfaces should be undertaken only if a lustrous surface is required by the type of measurements for which the electrode is being prepared, as in electro-optical studies, and then preference should be given to electropolishing. In the case of mechanical polishing, special care must be taken to remove all the polishing material from the electrode before it is placed in the cell.

Mechanical polishing of soft metals, such as lead, can result in small particles of the polishing material becoming embedded in the surface. In the case of electrode reactions involving solid phase formation, these particles can facilitate the crystallization of the reaction product, making previous nucleation unnecessary and thereby changing the reaction mechanism. For metals such as Pb, on which multilayers of product are formed in the electrochemical reaction, the danger of chemical contamination of the surface is not great when potentiodynamic sweeps are used for pre-treatment because the first sweep will remove the contaminated layer from the surface. The method of sealing a Pb-drop electrode under H_2 gives directly a mirror-like metal surface free from oxide contamination.⁽⁹⁾

2.2.3. Determination of the Real Surface Area

In the case of solid electrodes, no estimates of surface area can be made in terms of apparent geometrical dimensions unless the electrode surface is at least polished or, better, is prepared atomically smooth by ion bombardment in a high vacuum apparatus. The generally used BET method,⁽¹³⁾ based on

low-temperature adsorption of inert gases, requires very large surface areas for the measurements and can therefore only be used for specially prepared, large metallized electrodes, e.g., platinized platinum, or highly porous or powder electrodes, although modern gas desorption chromatographic techniques can give real area measurements down to $28 \text{ cm}^2 \text{ g}^{-1}$.⁽¹⁴⁾ In electrochemistry, the BET method is usually only used to confirm a new electrochemical surface estimation method.⁽¹⁵⁾ The assumption is then made, reasonably valid for electrosorption of small molecules such as hydrogen or oxygen, that the surface sites, available for physical gas adsorption, are the same as those which take part in the electrochemical reaction of interest.

No general electrochemical method for surface area determination, similar to BET, is available but, depending on the specific character of the electrode material, different electrochemical data can be used for surface area calculations based on one or more of the following:

- (i) The double-layer capacity value.
- (ii) The charge for electrochemical desorption of a monolayer of adsorbed H or O species.
- (iii) The values of diffusion-controlled currents for known species.

The estimation of surface area from the value of the double-layer capacity, first introduced by Frumkin,⁽¹⁶⁾ involves the assumption that the capacity of the double-layer is the same for different metals and corresponds, as for mercury, to $17\text{--}20 \mu\text{F cm}^{-2}$ and $40 \mu\text{F cm}^{-2}$, respectively, for the cation and anion adsorption regions. This is justified for high hydrogen overvoltage metals such as lead, thallium, tin, or bismuth, which exhibit double-layer behavior similar to that at mercury.⁽¹⁶⁾ However, on some metals, specific adsorption of ions and orientation of water dipoles differs from that at mercury and these effects may change the double-layer capacitance, compared with mercury, especially near the p.z.e., as was shown for Ga.^(17,18) For some noble metals, the absence of Faradaic electrochemical or adsorption processes in the potential range considered to be the so-called double-layer region has to be first proved. For example, at Ru, surface oxidation processes, which begin already at $+0.12 \text{ V/RHE}$, overlap with the H ionization process ($0.0\text{--}0.2 \text{ V}$). A double-layer charging process can, however, be resolved over a short potential range when strongly adsorbed anions, e.g., Br^- , are present.⁽¹⁹⁾

In the case of Pt and Rh electrodes, the estimation of the true surface area is usually based on an assumption, verified by BET measurements,^(15,20) that one atom of hydrogen is electrodeposited, or adsorbed from the gas phase, on each metal atom of the surface lattice, and that a monolayer of hydrogen is completed at the reversible potential of the hydrogen electrode.^(21,22) The charge associated with the underpotentially deposited monolayer of H can then be calculated from the length of the hydrogen segment of a charging curve⁽²¹⁾ or from a potentiodynamic $i\text{--}E$ profile by integration of the hydrogen region.⁽²³⁾

The small correction for the double-layer charge, amounting only to about 5–7% of the charge for monolayer formation,⁽¹⁵⁾ is made by taking the double-layer capacitance as constant in the entire potential range, and equal to the value for bare Pt in H₂SO₄ solution.

The charge for H monolayer formation on 1 cm² of the true surface, based on the number of metal atoms per cm², can only be calculated for surfaces of known crystallographic orientation. For polycrystalline wires or sheet electrodes, ambiguities arise with the crystallographic composition of the surface. Usually, for polycrystalline Pt surfaces, the value of 2.10 C m⁻²,^(21,24) corresponding to the value for the (100) plane, is arbitrarily taken, although some workers prefer somehow the higher value of 2.20 C m⁻².⁽²⁵⁾ In Table 3, the charges corresponding to formation of an H or O monolayer on various metal surfaces are given.

The true surface area at Pt electrodes is sometimes determined by means of a constant current anodic pulse from the charge passed in the linear part of the charging curve for metal oxidation before oxygen evolution commences at significant rates. In this method, proposed by Butler⁽²⁶⁾ and developed by Schuldiner and Roe,⁽²⁷⁾ it is assumed that, in the linear region, a monolayer of adsorbed oxygen is formed with one-to-one correspondence between platinum and oxygen atoms. Based on the same principle, the real surface areas of Pd,^(28,29) Ir, Rh, and Au⁽³⁰⁾ electrodes have been determined. Accord-

Table 3
H and O Monolayer Charges on Various Metals

Metal	No. of atoms on 1 cm ²	Charge of H monolayer, cm ⁻²	References
Pt (100)	1.31 × 10 ¹⁵	2.10	21, 24, 27
		2.08	22
Pt (111)	1.51 × 10 ¹⁵	2.42	27
		2.41	22
Pt (110)	0.93–0.92 × 10 ¹⁵	1.47 or 2.95	22, 27
Polycrystalline			
Pt	as on (100)	2.10	17, 21, 22, 27
		2.20	25
Ir	as on (100)	2.18	17
Rh	1.39 × 10 ¹⁵ as on (100)	2.20	15
		Charge of O monolayer, cm ⁻²	
Au		4.00	30, 31, 32
Ru		4.0	19
Pd	1.33 × 10 ¹⁵	4.2	28, 29
Ir		4.40	30

ing to Burshtein *et al.*,⁽³¹⁾ in 0.5 M H₂SO₄ the charge density of O-species in a potentiodynamic i - V profile, up to the minimum occurring before oxygen evolution, as shown in Figure 2, corresponds to 4.0 C m⁻², i.e., to one monolayer coverage with O-species. This value, which is obtained over a wide range of temperatures (298–365 K) and sweep rates (15 mV s⁻¹–48 V s⁻¹), was confirmed by the BET method.⁽³¹⁾

In the case of Au electrodes, the true surface area has also been determined from the double-layer charge and recently a very good agreement between the two methods was found for Au electrodes in 0.5 M H₂SO₄.⁽³²⁾

It has been suggested that during Pt oxidation, “dissolution” of oxygen in the top layer of the metal occurs and a “dermasorbed oxygen” film—a form of platinum–oxygen alloy—is produced which is not reduced in a subsequent

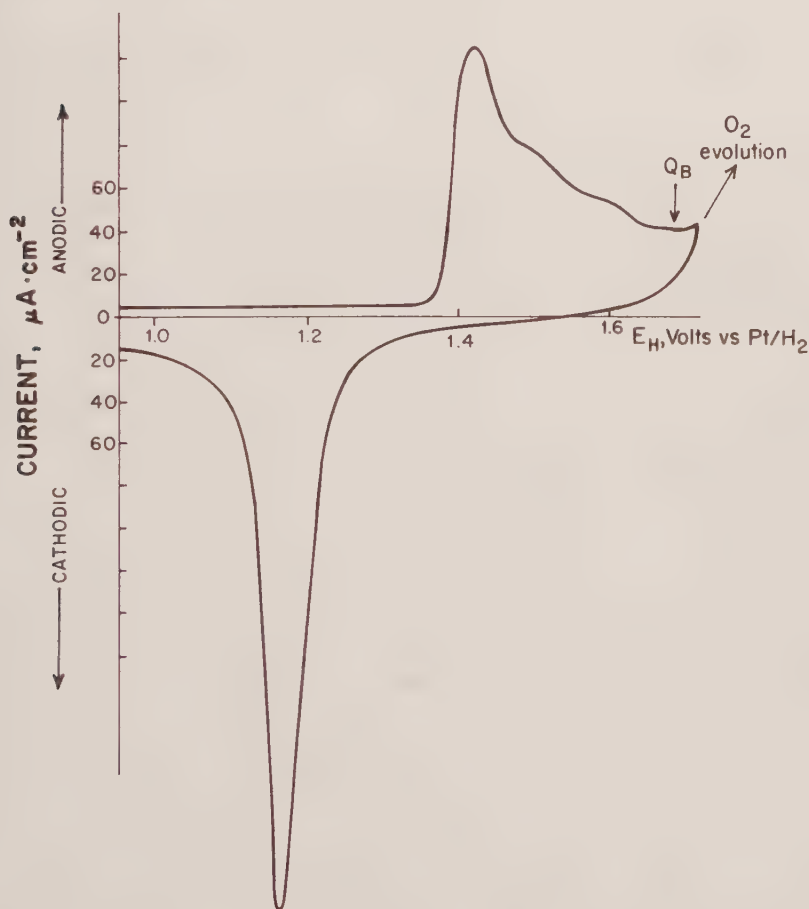


Figure 2. Potentiodynamic i - V profile for an Au electrode in 0.5 M H₂SO₄. ↓ “Burshtein minimum” corresponding to monolayer of electrodeposited O species.

cathodic transient, thus introducing a systematic error in evaluation of oxidation charges⁽³³⁾ for real surface area measurements. However, the failure by McIntyre and Kolb⁽³⁴⁾ to observe, using specular reflection spectroscopy, a residual film after oxide reduction provides strong evidence against the formation of such an oxygen alloy.

For well-defined mass-transfer conditions, the surface area of an electrode can also be estimated from studies of the limiting current passed in a diffusion-controlled reaction, when the diffusion coefficient of the diffusing electro-active rate-determining ion is known. The area of glassy carbon was, for example, evaluated in this way by Richards, Whitson, and Evans,⁽³⁵⁾ who measured the cyclic-voltammetric peak current for *p*-nitrotoluene reduction in acetonitrile with 0.1 M TBAP($[n\text{-Bu}]_4\text{N}^+\text{ClO}_4^-$) as supporting electrolyte. The diffusion-limited reduction current of potassium ferricyanide ($D = 7.67 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) in 1 M aqueous KCl is sometimes used to determine the real areas of Au and Pt electrodes.⁽³⁶⁻³⁷⁾

2.2.4. Stability of Electrode Surfaces

2.2.4.1. Roughening of the Electrode Surface

A polycrystalline noble metal electrode, subjected to anodic-cathodic treatments at slow sweep rates, does not suffer changes in its surface state or area even after days or weeks of experiments as long as the oxide coverage does not exceed one oxygen atom per metal atom in the surface lattice. However, when higher states of oxidation are reached, e.g., when a multilayer bulk type of oxide is formed, roughening of the surface can occur if fast sweeps, in particular rapid reduction sweeps, are used,^(32,38,39) as was first observed for Pt by Gilman⁽⁴⁰⁾ and later studied in detail by Biegler⁽³⁹⁾ and others. A rough surface obtained in this or other ways, e.g., by dissolution of an alloy component,⁽³²⁾ is unstable and will undergo a smoothening process when cycled more slowly.

If the smoothening process is prolonged, progressive rearrangement of the roughened surface occurs by a small amount each time a layer of surface oxide is formed; this brings the roughness factor down to about the value for a stable surface of minimum free energy. The driving force for the particle movement in the smoothening or roughening process is supplied, as first mentioned by Biegler,⁽⁴¹⁾ by the bond energy between the metal and oxygen.

It will be useful to summarize here briefly the main differences, which can be encountered in a potentiodynamic *i*-*E* profile for a Pt electrode, when the active surface of the electrode increases due to roughening or due to removal of adsorbed impurities. In both cases the currents corresponding to the hydrogen adsorption and ionization peaks will increase. In the roughening process, however, *all* the currents observed in both the hydrogen and oxide formation and reduction regions will increase in proportion to the increase of

the surface area. No change in the resolution of peaks or charge distribution will be seen. However, when cleaning of the surface⁽⁴²⁾ occurs (Figure 3), unblocking of the beginning of oxide growth and of the first hydrogen peak can be observed, and the hydrogen peak currents will change in a different way for every peak. Furthermore, the broad peak in the surface oxide formation region (due, partially, to oxidation of adsorbed organic impurities) will diminish with every oxidation–reduction cleaning cycle but, at the same time, the oxide *reduction* peak will increase, diminishing the charge ratio, Q_A/Q_C , for anodic and cathodic sweeps. The Q_A/Q_C will tend to approach unity for a clean surface. The decrease of Q_A accompanied by an increase of Q_C is also characteristic of the cleaning procedure at gold and other noble metal electrodes. Changes of the ratio Q_A/Q_C due to complications from oxide dissolution, corrosion, or difficulties with oxide reduction which arise on some metals,⁽⁴³⁾ when oxidation is carried out to charges higher than those corresponding to one monolayer of “MO,” should not be confused with the effects of the cleaning process.

2.2.4.2. Activation of an Electrode Surface

The process of cyclic oxidation and reduction, which enhances the electrocatalytic properties of noble metal electrodes, in particular Pt, (referred to in the sixties as “activation of an electrode”) was for a long time subject to controversy. Several theories were proposed. In earlier works,^(23,44–46) the increase in catalytic activity was attributed to surface rearrangement. At that time, however, the necessity for rigorous cleanliness of the whole electrochemical system was not fully recognized by many electrochemists. Recently it has been commonly agreed^(39,40,47–50) that most of the “activation” effects reported in the literature are due to removal of impurities from the electrode surface and to some roughening of the electrode, although some workers consider that surface restructuring on an atomic scale, other than roughening, also plays some role in the increase of catalytic activity of the electrode. Biegler,⁽³⁹⁾ for example, concluded that both removal of impurities and surface structural changes must be considered, but he wrongly ascribed to structural activation changes in hydrogen and OH adsorption peaks, typical for the cleaning process,⁽⁴²⁾ in which adsorbed impurities are removed and the H and OH electrosorption in various states is unblocked.

2.2.5. Single-crystal Electrodes

The use of single-crystal electrodes, particularly in surface reaction studies, to establish the relationship of surface processes to lattice properties is becoming more and more common.^(51–69) In earlier works, the single-crystal electrode surfaces were characterized only prior to a series of electrochemical measurements; despite the treatments to which the electrode was subjected, e.g., many

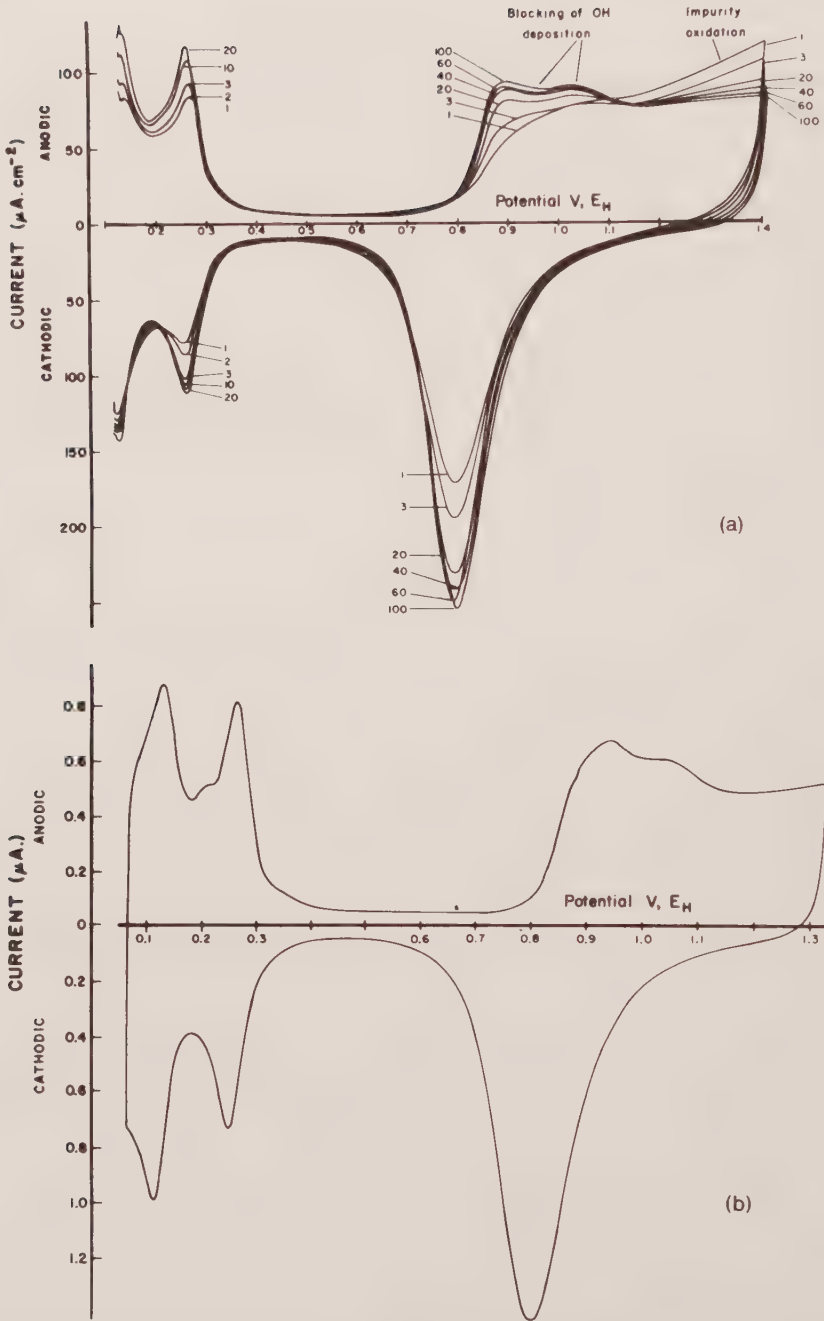


Figure 3. Potentiodynamic i - V profile for (a) dirty Pt electrode surface in 0.5 M H_2SO_4 . Cleaning of the surface by successive potentiodynamic sweeps; (b) clean Pt electrode.

cycles of oxidation and reduction, or even hot aqua regia treatment, the extent of roughening or faceting which may have occurred during electrochemical studies was not checked. Usually it was simply assumed that the crystallographic structure of the surface was maintained, at least to a sufficient extent that any effects of restructuring would not affect the results obtained.^(12,51-54,63-69)

Although the electrode surfaces were not perfect, they were predominantly of a certain crystallographic orientation so that, by comparison of results for predominantly different planes, some useful conclusions could sometimes be made concerning the influence, or lack of it, of crystallographic orientation on electrochemical reaction,^(52,53) on ion adsorption,⁽⁶³⁻⁶⁹⁾ and especially on the states of electrodeposited H and O species at Pt.^(51,54)

With the development and availability of ultra-high-vacuum apparatus, attempts were made to conduct electrochemical measurements in an arrangement of LEED–Auger–electrochemical systems.⁽⁵⁵⁻⁶²⁾ Since no presently available method for high-vacuum surface study of a metal can be applied while the surface is immersed in an electrolyte, the electrode must be transferred to or from the high-vacuum LEED–Auger chamber before and after electrochemical measurements or the electrolyte has to be brought in contact with the electrode in the apparatus, after release of the vacuum. Both these aspects of the technique present some experimental problems, especially in adsorption or monolayer studies since:

(i) Removal of an electrode from solution eliminates the potential control required for generation and maintenance of a definite state of the surface.

(ii) The transition, after characterization of the surface, from high-vacuum to normal pressure, resulted, in earlier work, in contamination of the surface with carbon. However, in some more recent works, this problem has been largely circumvented.^(55,56,60-62)

(iii) Vacuum pre-treatment techniques, usually ion bombardment, applied after electrochemical experiment may introduce changes in the state of the electrode surface to be examined.

(iv) Due to interaction with energetic electrons, during LEED or Auger measurements, distinct possibilities exist for surface alteration in the case of adsorbed layers or monolayers whose structures or compositions are to be examined. Reduction processes are obviously probable.

The results of early attempts to clean Pt single-crystal surfaces by ultra-high-vacuum techniques were unsatisfactory. It is only recently that, e.g., in the elegant work of Hubbard,^(55,60) an atomically clean, single-crystal surface of low index plane, after being cleaned by ion bombardment and characterized by LEED and Auger, was devacuumed without surface contamination, and put in contact with an electrolyte in a thin-layer cell situated inside the apparatus.

Several important conclusions for electrochemical experimentation can be drawn from this work: it was shown⁽⁵⁵⁾ that although the (100) Pt surface undergoes reconstruction in contact with water, changing from complex

symmetry to the (1×1) pattern, the surface does not change further when put in contact with acids. It can therefore be assumed that it will not undergo further reconstruction when other electrolytes are added. It was also proved⁽⁶⁰⁾ that the electrochemical results obtained at a Pt electrode removed from the vacuum apparatus and subjected to electrochemical reaction studies in a conventional cell do not differ from those which were obtained in the cell inside the vacuum apparatus. The latter conclusion justifies in further studies the simple procedure of characterizing the electrode surface before and after conventional electrochemical measurements without going into all the experimental difficulties of transferring the electrode from high-vacuum conditions to the cell in the LEED apparatus.

2.2.6. Mercury Electrodes

The ease with which mercury can be purified, the absence of surface structure problems encountered with solid electrodes, and the possibility of renewal of the surface *in situ* in most of the electrode arrangements for studies at mercury, makes this metal very convenient for kinetic studies. From all the various types of mercury electrodes, only the stationary mercury electrode, i.e., the hanging drop electrode (HMDE), will be discussed here; the dropping metal electrode, used in polarography, is outside the scope of this chapter.

The most serious difficulty, in the work with mercury electrodes, arises from the creeping of the electrolyte solution between the mercury and glass. This changes the accessible surface area of the electrode, causing poor reproducibility of the measurements and giving frequency-dependent capacitance results.^(70,71) Creeping can be prevented by hanging mercury drops from small Pt, Au, or Ag wires sealed in glass or by mechanically or electrochemically coating the wires with mercury. For reproducible results with the latter type of electrodes, the amount plated on support metals should be kept constant. Erroneous conclusions, especially in kinetic studies, can, however, arise due to dissolution of the supporting wire material in the thin-layer mercury coating. The amalgams so produced can form, in some cases, intermetallic compounds with the metal electrodeposited on the electrode in the reaction studied, leading to changes in the reaction mechanism. The danger of dissolution can be minimized in micro-mercury pool or sessile⁽⁷⁶⁾ drop electrodes, where only a very small Pt wire tip is in contact with the hanging mercury drop or small pool.

The most convenient mercury electrode for kinetic work is, however, the hanging mercury drop electrode (HMDE). Many mechanical arrangements have been designed to produce and keep the mercury drop of controlled size on the end of a silicone-coated glass capillary.⁽⁷³⁾ By means of a stainless steel micrometer screw⁽⁷⁴⁾ or piston⁽⁷⁵⁾ the drop can be pushed out from or pulled back into, the capillary from a tightly closed reservoir filled completely with mercury. Creeping of the electrolyte along the capillary walls is prevented by covering the glass with a hydrophobic silicone coating.⁽⁷⁰⁾ The strong adherence

of the drop to the tip of the capillary allows the drop to be rinsed with water or to be moved from one solution to another without danger of it becoming detached. The HMDE, as well as the Gerischer⁽⁷⁶⁾ hanging drop arrangements, gives the possibility for the drop to be renewed *in situ*.

Purification of mercury,⁽⁷⁷⁾ required in these types of experiments, usually consists in removal of dissolved amalgams by means of chemical pre-treatment by passage of a fine stream of mercury through a column of dilute nitric acid, followed by low-pressure triple distillation. Alternatively, an anodic electrolysis of a stirred pool of the mercury is recommended prior to distillation with an air leak (Hulett still) followed by double vacuum distillation.

2.3. Counter Electrodes

The counter electrode, whose only purpose in a cell is to allow passage of current, should function without introducing high resistance in the circuit or any new species in the solution which could interfere with the study of the process to be investigated at the other electrode. An electrode made from the same material as that to be used as the working electrode, and transferring current by the reverse of the investigated reaction, would therefore form the ideal counter electrode. In this way, no contaminants would originate from the counter electrode; under such conditions the electrolyte concentration in the cell would remain constant. However, it is not often that such a counter electrode can be found and used, although a process of this kind operates, e.g., in thin-layer cells⁽⁷⁸⁾ or in H_2 evolution experiments when H_2 gas is bubbled also through the counter electrode compartment at a catalytically active, stable anode. However, counter electrodes made from relatively inert materials such as Pt can usually be used with various working electrode materials if such an electrode is placed in a separate compartment. This arrangement serves to prevent the noble metal, which does usually dissolve in traces during anodic polarization,⁽⁷⁹⁾ from being redeposited on the working cathode and hence causing an alteration of its surface properties. Noble metals are usually dissolved only at potentials greater than the potential of formation of the corresponding surface oxide, indicating that it is not the metals but rather the oxides which undergo dissolution. According to Rand and Woods⁽⁷⁹⁾ the dissolution potentials in H_2SO_4 of oxides of various noble metals are as follows: Pt 1.07 V, Au 1.41 V, Pd 0.98 V, and Rh 0.67 V.

By using platinized platinum gauze for such an "inert" counter electrode, a large surface area is provided which minimizes the polarization of the electrode and the reaction resistance. When the working and counter electrodes are placed in one compartment, as is often required in electrochemical surface studies, the same metal as that used for the working electrode should definitely be used as the counter electrode. Therefore, with metals other than Pt, a Pt counter electrode should *not* be used owing to the possibility of contaminating the other metal test electrode.

The counter electrode should be prepared, cleaned, and mounted with the same care and in the same manner as is a working electrode, according to the recommendations given earlier in this chapter.

2.4. Reference Electrodes

In kinetic studies, the reference electrode is used not only to measure the potential of the investigated electrode but also in potentiostatic measurements as an element in the input channel of the potentiostat. Therefore, besides the usual requirements of stability and reproducibility of the electrode potential, an appropriate value of the impedance of the reference electrode is also required.

2.4.1. Choice of a Reference Electrode

The choice of a reference electrode is mainly one of convenience and compatibility with the chemistry of the system under investigation. There is a large variety of electrodes to choose from for aqueous and nonaqueous solvents, as described in the literature.⁽⁸⁰⁻⁸²⁾ When developing a new type of reference electrode, as is now often necessary for experiments in the many new solvents available, reference electrode reactions with high exchange current density and, for the “reversible” type (see page 34), with potentials dependent on concentration (activity) according to the Nernst equation, have to be chosen.

In selecting the most suitable reference electrode for a given system and type of measurement, the following factors, listed here in order of their importance, should be considered:

- (i) The chemical composition and stability of the reference electrode materials;
- (ii) The value of the electrode potential;
- (iii) The constancy and reproducibility of the potential; and
- (iv) The impedance of the electrode system.

Too often the importance of the first factor, the chemical composition of the reference electrode materials, is not properly recognized and the danger that contaminants may enter the test solution from the reference electrode is overlooked as, for example, in the use of the calomel electrode in some work on Pt and Au surface electrochemistry. To avoid contamination of the test solution, the reference electrode should preferably be reversible to an ion present in the test solution and made from the same materials as the working electrode. When a reference electrode made from substances foreign to the investigated system has to be used, special care should be taken to arrange good separation between the two systems by a closed ground-glass stopcock, additional electrolyte bridges, and proper design of the cell (see Section 4.1).

Besides these precautions, care should be taken (where chemically possible) to use the same solvent in the reference electrode as in the whole cell in order to avoid the introduction of an uncertain liquid junction potential across the interphase of the different solvents (see p. 39). Also, the following should be avoided in the reference electrode: (i) ions which can react with, or become adsorbed on, the working electrode, e.g., Cl^- , Br^- , I^- in the case of most working electrode metals; (ii) materials which can be reduced or oxidized in the potential range studied, and (iii) especially cations which can be electrodeposited on, or chemically displaced by, the working electrode material.

Therefore, the commonly used Hg or Ag based reference electrodes, especially of the second kind using, e.g., Hg_2Cl_2 , HgO , AgCl , may present a problem in work with other metals on account of the presence of halide ions, which can be specifically adsorbed on the working electrode, and of the possibility of poisoning the working electrode by deposition of Hg or Ag, when the potential range studied is cathodic for these metals.

The second factor is choice of the value of the reference electrode potential; if this is properly selected outside the potential range to be studied in the working electrode reaction, then an inconvenient change of sign of the reference voltage will be avoided during an experiment.

The third factor, the requirement for stability and reproducibility of the reference electrode potential, is less rigorous in kinetic studies than for the EMF measurements. A constancy better than several times the reproducibility of the test electrode potential is normally adequate. Since the reproducibility of potentials in solid electrode experiments is of the order of a few mV, a constancy of 1 mV for the reference electrode potential is usually sufficient and in some systems, especially in nonaqueous solutions, even a 2–4 mV shift of the potential during a longer run has to be tolerated. Such a small drift of the potential can easily be monitored against an independent reference electrode, and corrected.

The fourth factor, the impedance of the reversible electrode, is of great importance in fast potentiostatic transients. In particular, for surface reaction studies, the ohmic resistance of the electrode is a major factor of practical importance. The reference-to-working electrode loop is part of the input circuit of the potentiostat. The potentiostat power output provides voltage and current for the cell in the feedback loop, i.e., in the working-counter electrode circuit of the regulating system. The capacitive impedance of the electrodes causes a phase shift between the input and the output signals. This phase shift remains small when the resistances of the two loops are matched. The magnitude of the phase shift determines whether a negative or a positive feedback will result, i.e., whether the potentiostat will act properly as a regulator or will generate oscillations. In order to prevent the occurrence of instability or of oscillations in a potentiostatically regulated system, a proper ratio of resistances in the feedback current-carrying loop and the input loop of the potentiostat has to

be maintained, i.e., the resistances in the main cell (counter–working electrode connection) and that of the working-to-reference electrode connection have to be matched. This is especially important in the study of processes in which the reaction resistance at the working electrode can change over many decades in an experiment, e.g., when, in the study of surface processes at Pt, the potential changes from the highly reversible H adsorption region to the double-layer region having theoretically a reaction resistance equal to infinity. Also, in reactions where passivation sets in at some critical potential, with formation of resistive films, similar problems can arise.

This can be overcome to a great extent by addition to the system of a second, low impedance, reference electrode. In this dual reference arrangement^(83,84) the high impedance conventional electrode with the Luggin capillary with its characteristic high impedance is coupled by a resistor–capacitor combination with a low impedance, e.g., Pt wire electrode. For d.c. and low frequency currents the working electrode potential is kept constant with respect to the conventional reference, while the second electrode provides a low impedance path for high frequency components. At high frequencies the second electrode takes over the potential control. A properly chosen resistor–capacitor combination also acts as a line frequency filter.

2.4.2. Types of Reference Electrodes

The various types of reference electrodes commonly used in kinetic studies may generally be divided into three classes: the “reversible,” the “constant potential,” and the “internal” electrodes.

“Reversible” electrodes, which are made preferably, but not always, of the same material as that of the working electrode, are thermodynamically reversible to the same ions as those involved in the electrochemical reaction under study. Such an electrode is therefore, electrochemically speaking, part of the investigated system, and no liquid junction or foreign ions are involved. Under these conditions, any change in the concentration of the reacting or potential-determining ions (which are identical) will cause the reversible potentials of the reference electrode and the test electrode to change in the same manner. Therefore the potential measured against such an electrode does not include the Nernstian effect of ion concentration change; it includes only the kinetic effects and, if the reaction at the reference electrode is the same as that at the working electrode, the potential difference measured gives directly the reaction overvoltage.

It is nearly always possible to construct an appropriate reversible electrode for a particular system. For halide solutions, the silver/silver halide electrode⁽⁸²⁾ or mercury/mercurous halide electrodes are often used, especially for chloride solutions, for which the reversible calomel electrode is particularly convenient. For copper plating studies, the Cu/Cu²⁺ electrode has been used⁽⁸⁵⁾ but the most common reference electrode is the reversible hydrogen electrode,

RHE, used in studies of hydrogen and oxygen reactions, in formation or reduction of oxides, and for a variety of other reactions which have the same pH dependence as the hydrogen electrode. The hydrogen electrode has been used in aqueous, and in many nonaqueous⁽⁸³⁾ and mixed solvent⁽⁸³⁾ solutions. It is easy to prepare,^(82,86) convenient to operate, and its potential is usually very stable and well reproducible. The main restriction in the use of the RHE is that no species reducible by hydrogen can be present in the solution, e.g., metal ions which, when deposited on the platinized platinum, will poison the electrode, or redox couples which will establish erroneous potentials. The main disadvantage of the RHE is the necessity for bubbling hydrogen gas through the solution, but this can be avoided by use of the Pd-H electrode^(86,87) or the Giner⁽⁸⁸⁾ dynamic hydrogen electrode. The latter are thus well suited for measurements at high hydraulic pressures in closed systems⁽⁸⁶⁾ or otherwise in systems where gas bubbling is inconvenient.

A palladium hydride electrode, Pd-H, is convenient to use in a number of systems. It is made from a Pd wire or sphere charged with hydrogen to the region of coexistence of the α (solid solution) phase and the β (non-stoichiometric hydride Pd-H_{0.6}) phase, and exhibits a constant potential, independent of the total amount of H absorbed, so long as both phases are present.^(89,90) The potential of a Pd-H electrode thus formed has the same pH dependence as that of the hydrogen electrode and is 50 mV more positive⁽⁸⁹⁾ than the RHE at 298 K.

The temperature dependence of the Pd-H electrode potential is given^(91,92) by

$$E = (630.9 - 5.057 t^{\circ}\text{C}) \times 10^{-4} \text{ (V)}$$

The hydraulic pressure dependence of the individual potential for high pressures up to ca. 2500 bars has been derived⁽⁸⁷⁾ and is listed in Table 4.

The recent interest in high pressure kinetics makes it worthwhile to recall the Giner dynamic hydrogen electrode (DHE). A constant potential of the DHE is maintained by passing a small (1 mA cm⁻²) constant cathodic current at a platinized Pt electrode from an additional counter electrode placed above it. The evolved hydrogen creates a hydrogen electrode whose potential, due

Table 4
Pressure Coefficients of the Individual Potentials of Some
Electrode Processes^a

Electrode	$(\partial E / \partial P)_T, \mu\text{V bar}^{-1}$
$\text{H}^+ + \text{e} \rightleftharpoons 1/2 \text{H}_2$	-14.9
$\text{H}^+ + \text{e} + \text{Pd} \rightleftharpoons (\alpha + \beta) \text{PdH}$	-4.6
$\text{AgCl} + \text{e} \rightleftharpoons \text{Ag} + \text{Cl}^-$	-4.9

^a From Reference 87.

to a small overvoltage, is 20–40 mV more negative than the potential of the RHE. This overvoltage is, according to Giner,⁽⁸⁸⁾ constant with time, changing only less than 2 mV over 20 h. In nearly neutral, unbuffered solutions, a local pH change can be expected, causing a shift of the DHE potential to higher but also stable values. The exact value of the potential should therefore be checked against an independent reference electrode for every system. Although the pH dependence of the DHE potential is the same as that for a RHE, the dynamic electrode is obviously not a true reversible electrode. In a cell arrangement, the DHE is always located in a compartment separated from the main cell (see p. 37) to prevent gases evolved (O_2 as well as H_2) at the DHE from reaching the working electrode. As mentioned earlier, a DHE would be used only in special experimental situations where a freely bubbled H_2 electrode is inconvenient or is impossible to use, e.g., in a closed system.

The “constant potential” reference electrodes are self-contained half-cells of constant composition, independent of the investigated system and connected to the test cell by an electrolytic bridge. These reference electrodes are usually of the second kind, reversible to an anion. The main advantages of this type of electrode, viz. their high stability and the good reproducibility of their potentials, as well as their independence from the investigated system, are overshadowed in kinetic studies by the danger of contamination of the test solution by the components of the reference electrode materials, e.g., Hg, Cl^- , etc., and by complications arising from the relatively high electrical resistance of electrodes of this type. The two factors are interrelated because the means introduced to minimize the migration of the contaminating ions, such as long electrolytic bridges, closed ungreased stopcocks, etc., increase the resistance of the electrode arrangement. On the other hand, a cell design aiming at low resistance of the reference electrode–cell connection will not be adequate to prevent the contamination of the investigated system. These difficulties are of great importance in high-purity surface electrochemical studies.

The most commonly used “constant potential” reference half-cell is the calomel electrode (CE) ($Hg/Hg_2Cl_2/Cl^-$) in potassium chloride solutions of 0.1 and 3.5 mol dm⁻³, or saturated (SCE).⁽⁸²⁾ The CE potential, although very stable and reproducible at room temperature, exhibits a slow drift above 343 K due to disproportionation of mercurous chloride. There is also a lag in the potential adjustment after a change of temperature and hysteresis is observed on thermal cycling.⁽⁸⁴⁾ The salt bridge with KCl solution, usually used to join the CE with a test cell, eliminates the liquid junction potential only partially; therefore potential values listed in the literature include the small remaining liquid junction potential found under ordinary conditions. With change of pH, and in mixed or non-aqueous solvents in the cell, the liquid junction potential may vary considerably.

For maximum convenience, when alkaline or sulfate solutions are investigated, the $Hg/HgO/OH^-$ and the $Hg/Hg_2SO_4/H_2SO_4$ electrodes are often

used.⁽⁸²⁾ The silver chloride electrode is used mainly with hydrochloric acid (Ag/AgCl/HCl). Although it needs more elaborate preparation,⁽⁸²⁾ it is mechanically more stable and can be used without any hysteresis at higher temperatures than the CE.⁽⁹³⁾

An unpolarized metal wire in an aqueous solution will usually exhibit the potential of a surface oxide formed in air. This potential remains constant within a few mV over periods of many minutes and for some systems even for hours, making possible the use of such a wire as a practical "internal" reference electrode in potentiostatic transient measurements. This type of electrode is especially useful in experiments on noble metal behavior.^(4,94) Other surface layers, which can form on metal electrodes in the investigated solution besides oxides, may also be used. Such a reference electrode, when placed in the test solution at a minimal distance from the working electrode, will have a very low internal resistance and, due to proximity of the working electrode, the iR drop error will be small. Such "internal" reference electrodes are to be recommended primarily in studies of surface processes by transient methods at high rates and for experiments in dilute solutions where the resistance of solution bridges or other reference electrode junctions would be too high. The "internal" type of reference electrode is not a true thermodynamically reversible electrode; therefore its potential has to be separately measured and, due to possible drift, monitored during a run against an "external" true reference electrode.

Sometimes a characteristic feature of a transient, e.g., a peak, like those observed at Pt in an i - E profile of a potentiodynamic sweep, can be used to calibrate the potential scale. It has to be stressed that the "internal" reference electrode cannot be used when soluble electroactive products are formed at any of the polarized electrodes.

2.4.3. Construction of Reference Electrodes

The construction of a reference electrode varies with the type of the electrode used from just a wire next to the working electrode in the "internal" electrode type, through a special compartment divided from the working electrode compartment by a stopcock in a conventional three-compartment cell, to self-contained glass half-cells which are then connected by an electrolyte bridge to the cell.⁽⁸²⁾ At least two closed ground-glass stopcocks are then needed, one in the reference electrode bridge and one in the outlet tube of the cell. The internal resistances of such reference electrode arrangements increase in the order that the various types are listed above. The internal resistance of the last arrangement is quite high for non-steady-state kinetic measurements; therefore it is often used only for potential measurements when an "internal" electrode potential has to be monitored.

2.4.4. Reference Electrodes for Non-aqueous Systems

An extensive list of reference electrodes for nonaqueous systems can be found in the monograph by Mann and Barnes.⁽⁸¹⁾ Therefore only a few most commonly used electrodes, or electrodes employed in special systems, will be mentioned here.

The SCE can, in principle, be used in all those nonaqueous solvents in which Hg_2Cl_2 or Hg do not react with the solvent. Also, Hg_2Cl_2 must not undergo any disproportionation. Further, a soluble chloride must be found to replace the normally used KCl which has rather a limited range of solubility in most nonaqueous solvents. The predominantly used electrolytes are the lithium and the tetramethylammonium chlorides. LiCl has been used in calomel electrodes, e.g., in glacial acetic acid, ethylenediamine,⁽⁹⁵⁾ or propylene carbonate.⁽⁹⁶⁾ In the latter solvent, a 0.5 M solution gives a more stable CE potential than the saturated⁽⁹⁶⁾ salt solution. An even more stable and reproducible reference electrode in propylene carbonate is the saturated tetraethylammonium chloride (TEAC)/calomel electrode^(97,98) and is especially convenient because the temperature dependence of the electrode potential is known.⁽⁹⁸⁾ The aqueous SCE is also often used with nonaqueous systems, but the unknown and undefined liquid-junction potential at the interface of water and the nonaqueous solvent makes this practice rather unsatisfactory. Also, the slow diffusion of some water into the nonaqueous solution will occur and introduce undesirable effects in most cases, e.g., with alkali metal electrodes. Another popular and commercially available SCE of the same type is the alcoholic potassium chloride/ Hg_2Cl_2 electrode, which may be used with some amphiprotic and aprotic media with which water is not readily miscible but alcohol is. Calomel electrodes cannot, however, be used in acetonitrile, *N,N*-dimethylformamide, or dimethylsulfoxide because Hg_2Cl_2 disproportionates in these solvents.⁽⁸³⁾

The silver electrodes, frequently used in aqueous solutions, are often unsuitable: the Ag/AgCl for acetonitrile, dimethylsulfoxide, *N*-methylacetamide,⁽⁸³⁾ and propylene carbonate,⁽⁹⁹⁾ because soluble silver chloride complexes are formed in these solvents and the Ag/ Ag^+ electrode for *N,N*-dimethylformamide (DMF) because Ag^+ is reduced by the solvent,⁽⁸³⁾ although some authors report a stable potential for this electrode in DMF.^(85,86) The silver/silver ion electrode is also not stable in pyridine over long periods of time.⁽¹⁰⁰⁾ In many other solvents,⁽⁸³⁾ however, the Ag/ Ag^+ electrode, with a fixed concentration of silver ions, does make a very good reference electrode.⁽¹⁰¹⁾ With constant concentration of 0.01 M of Ag^+ and 0.1 M tetraethylammonium perchlorate, it is the most commonly used reference electrode in acetonitrile.⁽¹⁰²⁾ The electrode potential is 0.293 V against aqueous SCE.^(103,104) A similar silver electrode has also been used in propylene carbonate⁽¹⁰⁵⁾ and in sulfolane.⁽¹⁰⁶⁾ Because of the presence of silver ions in the solution in these electrodes, the reference electrode has to be in a separated compartment in the cell.

The silver/silver chloride electrode is reported to be stable in acetone-water mixtures up to 95% for weeks and even in anhydrous acetone it can be used for a few hours.⁽¹⁰⁷⁾ A Ag/AgI electrode in tetrabutylammonium iodide (TBAI) works well in DMF.⁽¹⁰⁴⁾ In DMF, a Cd/CdCl₂ electrode was also used as a reference electrode⁽¹⁰⁸⁾ and in propylene carbonate the systems Li/LiClO₄⁽¹⁰⁹⁾ and Tl(Hg)/TlCl/LiCl⁽¹¹⁰⁾ were found to have suitable properties as reference electrodes.

The platinized Pt hydrogen electrode functions properly in many nonaqueous solvents or their mixtures with water provided that no catalytic reduction can occur. Thus the H₂ and the PdH electrode functions in many anhydrous solvents, e.g., alcohols, formic, acetic and trifluoroacetic acids,⁽¹¹¹⁾ and in HF.^(112,113) The electrode can also be used in propylene carbonate in the presence of HClO₄ or trifluoromethanesulfonic acid.^(114,115) In HF the Cu/CuF₂/KF electrode has also been employed as a reference electrode.⁽¹¹³⁾

In thionylchloride, a lithium-lithium tetrachloroaluminate reference electrode has a very stable and reproducible potential and small reaction resistance,⁽¹¹⁶⁾ and for aromatic hydrocarbons, Al in solutions of AlBr₃ and KBr was used as a reference electrode for cyclic-voltammetry.⁽¹¹⁷⁾

Recently, some chemically modified electrodes have conveniently been employed as reference electrodes. A Pt electrode with electrodeposited polyvinylferrocene (PVF) film can be used as a useful reference electrode in acetonitrile and the potential of the half-oxidized electrode is 0.39 V against the SCE.⁽¹¹⁸⁾ Other polymer electrodes with lower solubility of oxidized and reduced states than PVF may be useful in a wider range of solvents.⁽¹¹⁸⁾

Also some ion-selective electrodes (H.R.E.F.) (Orion Co) could be used in certain nonaqueous media as reference electrodes.

2.4.5. Comparison of Potential Scales in Various Solvents

The aqueous SCE is often used as a reference electrode also in nonaqueous solvents providing a supposed common reference scale for the various systems.⁽⁸³⁾ The measured potential difference includes, however, an unknown and sometimes irreproducible liquid-junction potential between the aqueous and nonaqueous solution phases, making the potential scale arbitrary. Furthermore, when the aqueous SCE is employed, contamination of the anhydrous test solution by water and K⁺ or Cl⁻ ions can easily occur.

A proper common potential scale would require a reference redox couple which does not involve interactions with solvents, and would therefore give a reference potential independent of the nature and composition of the solvent. The Rb/Rb⁺ couple^(119,120) was used extensively for this purpose, but its potential, as was found later, is not truly invariant with solvent^(83,121) as might be expected due to solvation of Rb⁺. Therefore, according to a suggestion made by Strehlow,⁽¹²²⁾ the oxidation potential of ferrocene [Fe(C₅H₅)₂] is now

used as an intersolvent reference. However, the problem arises^(113,123,124) that ferrocene may undergo protonation in strong acidic media. Thus, recently a different electrode was developed on the basis of the electrochemical behavior of polynuclear aromatic hydrocarbons,⁽¹²⁵⁾ such as perylene, and has a potential independent of solution composition over a wider range of solvents⁽¹²⁴⁾ than has ferrocene. Such an electrode has been used in highly acidic media such as water-H₂SO₄ mixtures,⁽¹²⁴⁾ trifluoromethanesulfonic acid,⁽¹²⁶⁾ and HF.⁽¹²⁷⁾

3. Electrolyte

3.1. Choice of Electrolyte

The main role of the supporting electrolyte in an electrochemical cell is to conduct currents and to dissolve the electroactive species. Therefore both components of the supporting electrolyte, i.e., the solvent and current-carrying solute, should not be reactive chemically or electrochemically in the system studied, nor over the potential range of the particular experiments. Exceptions arise when the solvent or the current-carrying solute are also the electrochemical reagents.

Although the supporting electrolyte does not take part in electrode reactions, the ionic composition of the electrolyte may influence the electrode kinetics due to the presence of anions and cations in the double-layer and due to adsorption at the electrode of many of the anions. The adsorbability of the commonly used anions increases on most electrode materials in the order $F^- < ClO_4^- < NO_3^- < HSO_4^- < Cl^- < Br^- < I^-$ with the last two ions often forming rather a monolayer of surface compound when they become adsorbed.⁽¹²⁸⁾

Usually inorganic salts dissolve better in water than in organic solvents, while organic salts dissolve better in organic solvents. The solubility of salts in a particular solvent can be increased by mixing solvents having similar electrochemical behavior but different dissolving power, e.g., by adding alcohol to water which will increase the solubility of most organic compounds, or by complexation of otherwise simple ions as is done with Li⁺ salts in nonaqueous aprotic solvents in Li-battery technology.

As supporting electrolytes for nonaqueous solvents, the aliphatic quaternary ammonium salts are very suitable, especially the tetra-*n*-propyl- and tetra-*n*-butylammonium salts as they cannot be oxidized electrochemically and are reduced only at high cathodic potentials. For work at high anodic potentials, tetrafluoroborates, hexafluoroantimonates, and sometimes trifluoroacetates may be used. The anions more often used are perchlorates, nitrates, or halides but the latter may cause problems because they are easily oxidized and adsorb on most metals.

3.2. Characteristics of Solvents

The dielectric constants of most non-aqueous solvents are much smaller than that of water, making it difficult to find salts soluble in these solvents. Amongst the most useful and frequently employed organic solvents, only propylene carbonate with $\epsilon = 69$ at room temperature has a value comparable with the high value for water (78 at room temperature). To ensure dissociative dissolution of the solute, a dielectric constant of 10 or more is needed for the solvent.

The working potential range in a given solvent is restricted by solvent or supporting electrolyte decomposition. For water, the most commonly used solvent, the working potential range is limited by the potentials of thermodynamic stability of water practically to about 1.3 V. It can be extended in either direction only for electrodes on which hydrogen or oxygen evolution are kinetically hindered. For electrocatalytic reactions, the working potential range is practically even smaller than 1.3 V, due, in the positive direction of potentials, to oxide formation which occurs, even at noble metals, at potentials less positive than those for oxygen evolution. At some metals on the negative side, a similar limitation arises because of underpotential deposition of H.⁽¹²⁹⁾ Electrodes of most non-noble metals are always covered with an oxide film when in contact with water.

To obtain a wider working potential range or to study reactions on oxide-free surfaces, non-aqueous aprotic solvents with decomposition potentials higher than that of water are used. This makes possible the deposition or study of reactions of very electronegative elements, e.g., Na or Li, or very electropositive ones, e.g., F₂.

The most common solvents with good anodic working potential range are acetonitrile (AN), trifluoroacetic acid (TFA), nitromethane, and benzonitrile. Dimethyl- and diethylformamide (DMF and DEF) and also dimethylacetamide (DMA) represent solvents having high cathodic decomposition potentials. An extended anodic and cathodic range can be achieved in propylene carbonate and in completely anhydrous benzonitrile.

The use of aprotic solvents also usually allows the immediate products of electron transfer in the reduction or oxidation of organic substances to remain unchanged for significant lifetimes, e.g., without suffering annihilation by H or OH transfer, as in the case of electrolytically generated carbonium ions or carbanions produced, e.g., in electrochemiluminescence or in some organic electrosynthesis reactions.

3.3. Methods of Purification

3.3.1. Impurities in the Electrolyte

The main types of impurities which, when present in electrolytes, even in traces, will interfere with electrochemical measurements are: (a) metal

cations which, when they become electroplated on an electrode, cause changes to its catalytic properties and (b) adsorbable anions or organic compounds which may block the electrode surface for the reaction studied. If the adsorbed or other impurities are electroactive over the potential region to be experimentally investigated, they can generate oxidation-reduction currents which may interfere with the observation of the proper reaction current. This will be specially noticeable in transient measurements.

In an electrochemical system, the solvent is usually the main source of impurities (see Table 1, page 17) primarily because of the abundance of the solvent since, in a conventional cell, the electrode surface area-to-solution volume ratio is of the order of 1 : 100. The current-supporting species and the reacting substances can seldom be traced as the source of impurities. "Analytical" grades of acid can usually be used without further purification but, if necessary, some acids can be further cleaned by normal or vacuum distillation. Single or repeated recrystallization of salts from solvents of the same degree of cleanliness as that of the solvent to be used later in the cell, is nearly always adequate. In some cases, calcination in an electric oven is used to remove organic impurities from inorganic substances.

For solvent purification, general methods such as distillation, fractional freezing or chemical treatments are used.⁽¹³⁰⁾ These purification techniques may not be sufficient; therefore a final removal of impurities by *in situ* pre-electrolysis or by refluxing the supporting electrolyte through purified charcoal may be necessary. According to the present author's experience, these procedures are not needed for aqueous solutions made with pyrodistilled water⁽⁴²⁾ prepared as described in Section 3.3.2. Passage of the solution to be purified through a chromatographic column filled with adsorbent is also sometimes used.⁽¹³¹⁾

In non-aqueous systems, the main common impurity which can change drastically the kinetics and even the mechanism of the reaction studied is water. The removal of traces of water from the solvent and from the walls of containers or cells where water is always adsorbed is achieved either by reacting the water chemically by adding, e.g., an acid anhydride⁽¹²⁸⁾ to the acid, as in the case of CF_3COOH , or the traces of water are "washed out" by a clean, water-free solvent in a closed system. Water adsorbed on glass or metal walls is also often removed by heating the walls and flushing the heated system with a dry inert gas. All the operations with nonaqueous systems should usually be carried out in a dry box. The content of water in solutions can be determined by the Karl Fisher method.^(132,133)

3.3.2. Water Purification

Some contaminants found in recent years in water supplies are not oxidizable by boiling with alkaline permanganate in the normal water purification procedure. The species are not retained by alkali on distillation, and, being

steam volatile, appear in the distillate. However, these impurities can be removed by catalytic oxidation on Pt at high temperature in the vapor phase. The apparatus for catalytic pyrodistillation⁽⁴²⁾ developed in this laboratory is shown in Figure 4. The impurities from the double-distilled water (1) (used as the input supply) are oxidized catalytically by purified O₂ (2) which passes

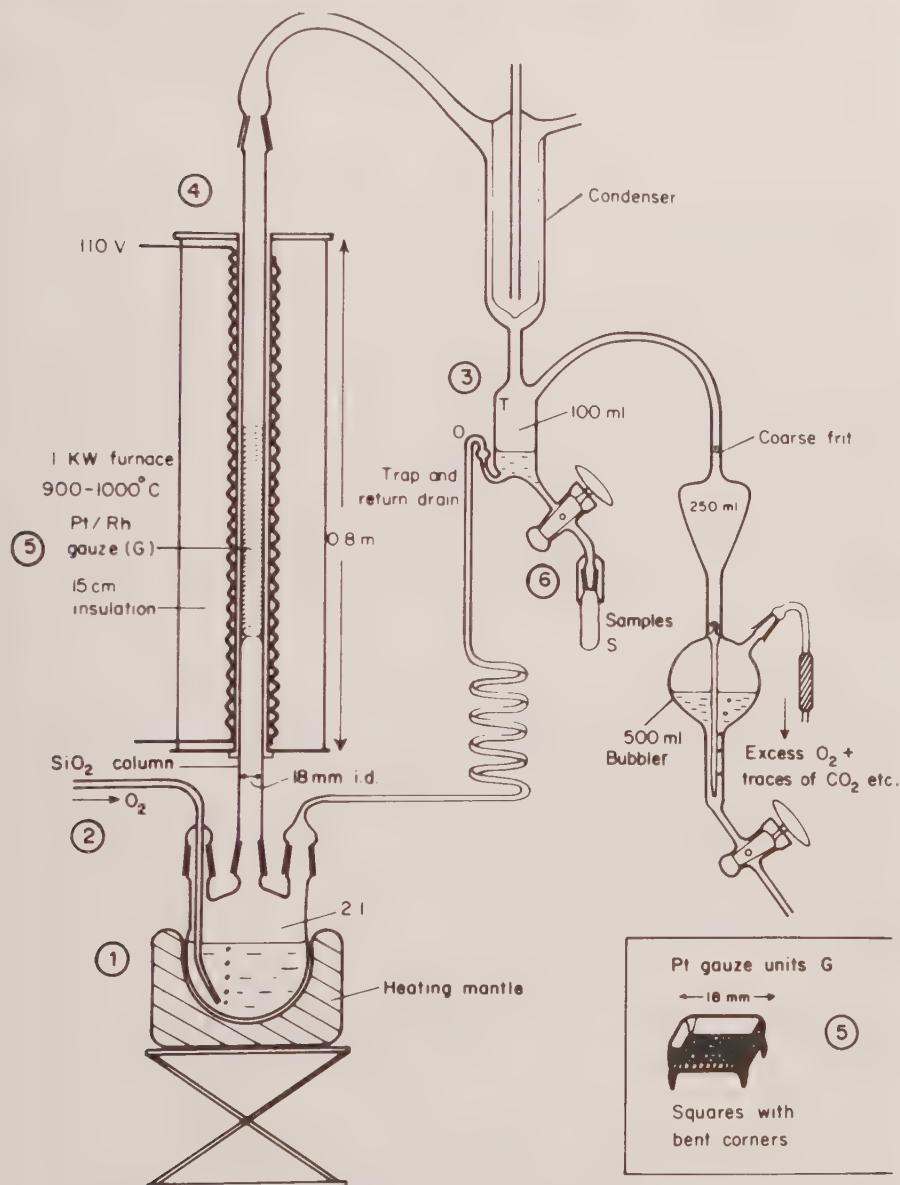


Figure 4. The apparatus for catalytic pyrodistillation of water.⁽¹³¹⁾

with the water steam in a recycling system (3) through a silica column (4) containing 90% Pt/10% Rh gauze baffles (5) heated to 750–800°C. The apparatus is operated so as to recycle the water through the catalyst furnace for 48 h before the water is collected (6). In order to avoid the possibility of the presence of traces of Pt in the pyrodistilled water arising from volatile, hydrothermally formed products of the catalyst, a further regular distillation is advisable for work at electrodes other than Pt. The solutions made with pyrodistilled water pass the most rigorous cleanliness tests,⁽⁴²⁾ and the pyrodistillation apparatus is easy to operate and can be used constantly for years.

The purification of water by catalytic pyrodistillation is thought to be essentially superior to methods based on adsorption of impurities by circulation of the solution through a column of active charcoal^(134,135) or platinized Pt sponge potentiostated near the p.z.c. for a period of hours or days.^(136,137) Adsorption methods are time-consuming procedures and involve the difficulty of obtaining and maintaining the adsorbent in an ultra-pure condition. In the case of charcoal, for example, at least six-months processing is needed first by continuous Soxhlet extraction with HCl until the extract remains colorless and then with distilled water until the extract gives no test for Cl^- .⁽¹³⁸⁾

In these methods there is also no indication of saturation of the sorbent other than the appearance of the undesired impurities in the purified water. For electrochemical systems not sensitive to impurities, double-distilled water may still be adequate, e.g., for studies where current densities are large or where bulk materials as in battery electrodes are to be studied.

3.3.3. Pre-electrolysis

The removal of oxidizable or reducible impurities by pre-electrolysis of the electrolyte on a sacrificial anode or cathode was first applied by Lewis and Jackson⁽¹³⁹⁾ in 1906. It was later used extensively by Frumkin and his school and, in the fifties, the conditions for effective pre-electrolysis were studied both experimentally and theoretically by Azzam, Bockris, Conway and Rosenberg,⁽²⁾ and later reviewed by Bockris.⁽¹³⁶⁾ Pre-electrolysis became a general practice for about twenty years. This technique, which is based on diffusion-controlled deposition, or oxidation/reduction of impurities, is most desirable when continuous Faradaic processes are studied over some hours, especially in the case of a cathodic process such as H_2 evolution when traces of cation metal impurities may be electrodeposited and modify, even at sub-monolayer coverage, the catalytic properties of the electrode surface.

The pre-electrolysis is best carried out from 24 to 48 h at potentials sufficient to oxidize or reduce the impurities diffusing to the large sacrificial electrode but low enough not to dissolve the electrode or decompose the solvent or supporting electrolyte. When the type of impurities present is not

known, the pre-electrolysis potential is maintained at the highest value which will be used in the subsequent experimental measurements. The sacrificial electrode should be removed from the solution at the pre-electrolysis potential to prevent desorption or dissolution of the deposited impurities.

Nowadays the use of pre-electrolysis is mostly abandoned because, as was observed by Breiter⁽¹⁴⁰⁾ and others, the solutions purified with today's cleaning methods, especially water solutions, will not improve further through pre-electrolysis.

3.3.4. Criteria for Solution Purity

Generally the following effects, when observed in an electrochemical system, indicate the presence of impurities:

- (i) the lack of reproducibility of measurements and of consistency of results;
- (ii) time effects not expected in the reaction studied; and
- (iii) stirring effects in an otherwise non-diffusion-controlled reaction system.

As the level of cleanliness needed in a particular system depends on the type of measurements which will be later performed on it, the test method must also be related to the type of final studies involved. For capacitance measurements, for example, the value and the constancy of the double-layer differential capacitance near the p.z.c. will be indicative of the cleanliness of the system; for kinetic studies, the constancy of overpotential. For both types of measurements, the conductivity of water used for preparation of the solution cannot normally be used as a measure to determine the level of impurities which will interfere with the subsequent measurements since the presence of non-conducting organic species adsorbable on the electrode surface will not increase the conductance of water, although it may dramatically change the kinetics of the electrochemical reaction and modify the double-layer capacitance.

A very sensitive method for detection of the presence of adsorbable organic species or anions, and of ions which can be plated out on an electrode, is the study of the potentiodynamic current-potential profiles for H or O-species underpotential deposition at Pt electrodes in mineral acid solutions. Very strict criteria for a clean solution have been given by Conway *et al.*^(42,141,142) on the basis and even more rigorous ones are used by Furuya and Motoo.⁽¹⁴³⁾

On the basis of the first work,⁽⁴²⁾ the following criteria were established to confirm the purity of a Pt electrode-solution system:

- (i) Absence of any effects of stirring on the i - V profile;

- (ii) Absence of any slant of the profile about the zero current line, due to Faradaic oxidation processes at positive potentials and Faradaic reduction processes at the negative end of the sweep;
- (iii) Absence of any spurious peaks in the double-layer regions of the sweep;
- (iv) Resolution of the multiple H and O peaks and maintenance of the shape of the profile down to very low sweep rates (0.005 V s^{-1});
- (v) Equality of anodic and cathodic charge in the potentiodynamic sweep to within 2%;
- (vi) Constancy of the H deposition and desorption charges to within 5% of their original values for at least 1 h while the potential range used *excludes* the O-species deposition region.

Constancy of the hydrogen adsorption region after holding the potential of the electrode at 0.05 V or 0.80 V for several hours was used as a cleanliness test by Furuya and Motoo.⁽¹⁴³⁾

The linearity of the voltage vs. time relation in a constant-current charging curve in the oxygen adsorption region on Pt electrodes in 1 M H_2SO_4 could also be used according to Schuldiner *et al.*⁽³⁾ as a reliable identification of electrode cleanliness. This method is, however, less sensitive than the differential method of potentiodynamic sweeps.

3.3.5. Degrees of Purification Required

The impurity level which can be tolerated in electrode-kinetic studies can be estimated by means of a simple calculation: 1 cm^2 of a metal surface which consists of ca. 10^{15} atoms will be completely blocked by adsorption of 2×10^{-9} mole of small molecules which occupy one adsorption site per molecule. Depending on the ratio of electrode surface to solution volume, the complete blocking of surface sites will occur at different concentrations. For the usual surface-to-volume ratio of 1:100, a concentration of $2 \times 10^{-8} \text{ M}$ of impurities will block 100% of the electrode but even 10% of coverage, i.e., from a $2 \times 10^{-9} \text{ M}$ solution, may alter the kinetic process substantially, especially if larger molecules requiring few sites per molecule are reacting in the kinetic process under study. By diminishing the solution volume or increasing the geometrical or real electrode surface, whichever is experimentally more convenient, the tolerance for impurity concentration may be increased. Since the process of blocking the electrode surface is diffusion-controlled in measurements in which the testing program includes the removal of impurities, or by oxidation or by desorption when the p.z.c. is crossed, higher levels of impurities can be accepted. Higher levels of impurities can also be tolerated for measurements on metals covered with oxide films because of the self-cleaning ability of oxides to oxidize the impurities off the electrode.

4. Cells

4.1. General Requirements for Cell Design

An individual cell with special features is usually designed for each particular type of measurement but, for a successful work, several general requirements in cell design have to be met:

- (i) The cell has to be easy to handle and easy to clean;
- (ii) The design of the cell should include provision for protection of the cell solution from the ingress of external impurities and the solution of the working electrode compartment from the species involved in the counter and reference electrode compartments, when the necessity exists to separate these compartments;
- (iii) To minimize the effect of impurities, a high ratio of surface area of the working electrode to solution volume is preferred;
- (iv) The material of the cell should, of course, be as unreactive with the cell solution as possible;
- (v) A low ratio of surface area of the cell walls to the volume of the solution is desirable to prevent any species which may be leached out from the cell walls to attain a substantial concentration;
- (vi) As the solution, and particularly the solvent, is usually the main source of impurities in an electrochemical system, the volume of the solution should be kept to the minimum required to ensure constant and convenient conditions during measurements; and
- (vii) It is very important to ensure that the solution in the cell does not close off any air pockets, from which air can only be removed by diffusion and thence cause depolarization at the cathodes during measurements.

The size of the cell is usually determined by the volume of the solution needed. Larger cells are therefore used when constant Faradaic currents are passed as in polarization curve studies. Cells with small or very small volumes can be used when the reverse of the working electrode reaction occurs on the counter electrode, as, e.g., in thin layer cells,⁽⁸⁰⁾ or when, on the working electrode, a reaction occurs in the forward and backward direction shifted in time as, e.g., in cyclic-voltammetry studies of surface reactions on noble metals.

The use of large three-compartment cells, suitable for long-duration, continuous electrochemical reactions, was described in detail in the fifties⁽¹⁴⁴⁾ and early sixties.^(145,146) Since up to six individual working electrodes can be used in a given purified solution without opening the cell, this type of cell is well suited for work with nonaqueous solutions. However, such large complicated cells are rather difficult to clean. A cell which can be dismantled into simple small parts, which can then be handled separately when cleaned, is preferred, despite the many joints or fittings which it has to have, over a big complicated rigid assembly.

The danger of contamination through the fittings can be minimized by correct design (see below) or by placing the whole cell in a plastic tent kept under a neutral gas atmosphere.

In order to minimize the intrusion of impurities from the surroundings into the cell, the cell ground-glass joints or fittings, in cells made from other materials than glass, have to be always mounted in such an orientation that a drop of solution put on a joint, after wetting it, will leave the cell (Figure 5b) and not fall into it (Figure 5a).

In a glass cell, well designed for high purity work, contact between the electrolyte and ground glass should be as small as possible, or preferably absent, as every ground-glass surface, due to capillary openings and fine-grained structure, is a source of impurities which cannot be washed out completely and which will slowly diffuse out into the solution during measurements. This is specially damaging when small electrodes and a small volume of electrolyte are used because of the unfavorable ratio of the strongly developed ground-glass surface to the small volume of the solution (point V, p. 47).

A complete absence of contact between the ground glass and the solution may be achieved in a one-compartment cell as shown in Figure 6. The cell in Figure 6 is equipped with an additional connecting tube A, which allows the potential of the internal reference electrode to be monitored by an auxiliary reference electrode. Such cells are used mainly for studies of surface reactions when no soluble products are formed at the electrodes. In conventional 2- or 3-compartment glass cells, an ungreased ground-glass stopcock between the working and counter electrode and/or the working and reference electrode compartments cannot be avoided as the necessary electrical contact has to be provided between these compartments.

Instead of glass stopcocks, sintered glass or porous Vycor separators may be placed between the cell compartments but, because they cannot be washed free of impurities, their use should be restricted to systems proven to be insensitive to impurities due to the nature of the electrochemical reaction or due to the use of a large volume of electrolyte and large electrodes. For high current measurements, polymer membranes, e.g., of the Nafion type, may become useful in non-glass cells of the sandwich type. However, it is rather

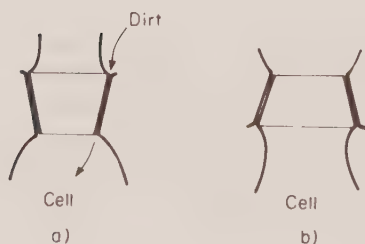


Figure 5. Mounting of ground-glass joint: (a) the wrong way; (b) the right way.

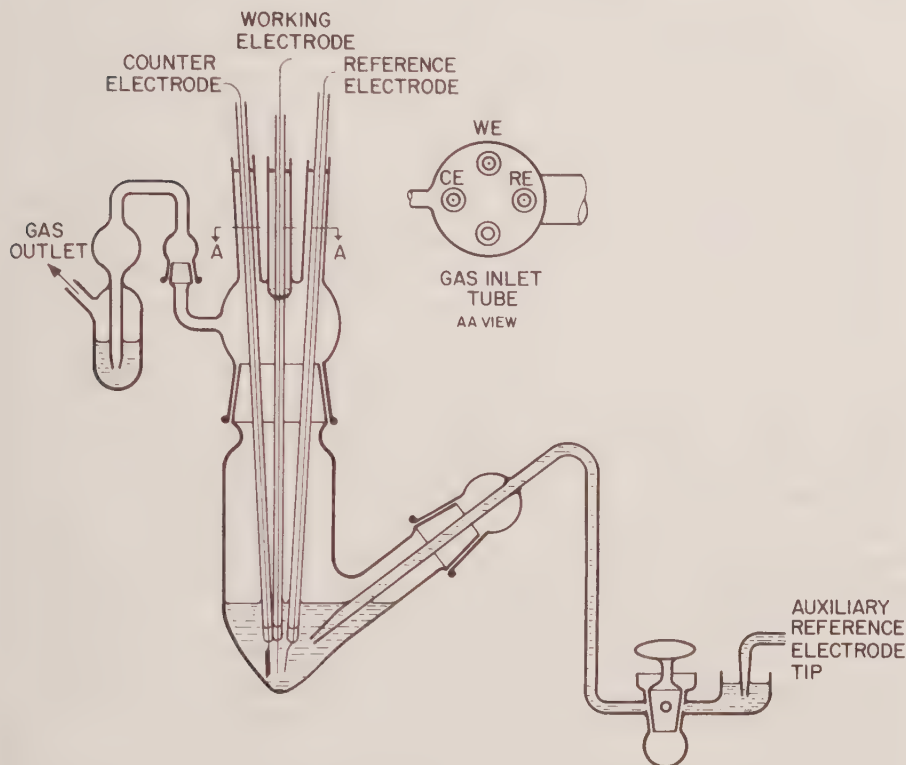


Figure 6. One-compartment cell.

inconvenient to mount membranes into glass cells, although cells with flange joints, sealed by O-rings, are sometimes used.

Contamination of the working electrode by impurities originating from the reference electrode or counter electrode compartments can be diminished by keeping the solution level in the working compartment always above the solution levels of the other compartments, so that the syphonic forces work in the direction away from the working electrode.

This is specially important for the connection between the working and reference electrode compartments when the connecting tube is the Luggin capillary. Since the end of the Luggin capillary is always placed near the working electrode and points at it, all the impurities which may come from the tube, including foreign ions from the reference electrode, if any are present there, will tend to diffuse straight onto the working electrode surface. Therefore, the cell design often used in which the reference electrode is placed *above* the working electrode compartment should be avoided.

To ensure the right position with respect to the Luggin capillary or with respect to each other, the electrodes in the main cell compartment can normally be freely rotated and shifted vertically by mounting them on smooth glass sliding tubes (obtainable from Eck and Krebs Co., New York), sealed by Teflon O-rings, screwcaps, or Teflon tape. The electrodes in reference and counter electrode compartments are usually sealed or mounted permanently into the upper part of the cell compartment caps.

To speed up the outgassing of the cell, the gas bubbler should reach near to the bottom of the cell, but the gas bubbles which diminish the conducting cross section of the solution should not go straight onto the electrodes or between them.

In fast transient measurements, for which high currents are required, the resistance of a stopcock separating the electrode compartments or of a glass frit may be too high; then a one-compartment cell has to be used. To avoid complications from traces of counter electrode material being deposited on the working electrode the former should be made, if possible, from the same material as that of the working electrode. When noble metals are used as the material for the counter electrode, the possibility that they may dissolve in trace amounts has to be considered as it is well known⁽⁸¹⁾ that the noble metals corrode on anodic polarization or when chlorine is evolved on them.

Special criteria for an electrochemical cell to be used for investigation of fast reaction by means of potentiostatic transients are given by Cahan *et al.*⁽¹⁴⁷⁾ while Harrar *et al.*⁽¹⁴⁸⁾ discuss the frequency limitations arising out of cell design.

The final design of a cell will always be the result of a compromise between the special requirements of the particular system or type of measurement and the strict demand for cleanliness. For less sensitive work some rules can be relaxed and it is up to the researcher to establish the right balance. Much earlier work, except that of the Russian school, was vitiated by lack of attention to or realization of these requirements.

4.2. Materials

4.2.1. Glasses

Despite the many new materials available for construction of electrochemical cells, glass is still the most convenient and most often used, and chemically the most satisfactory. The important technical advantages which make glass so suitable as the construction material in electrochemical work are its electrical insulating power, high chemical resistance, impermeability, and transparency. They outweigh the main disadvantages of glass, e.g., its low resistance to the action of alkalis and HF, and its fragility and low thermal conductivity which can lead, when the coefficient of expansion is high, to low thermal shock resistance.

Generally glasses are resistant to attack by water and most water solutions, by organic solvents, by acids even when hot, except for hydrofluoric acid at all temperatures and phosphoric acid above 150°C. Glasses are attacked by alkaline solutions, the attack increasing with concentration of alkali in solution and with temperature, as well as with concentration of silica in the glass, making quartz, the fused silica, the least resistant.

Since glass consists mainly of silica fused with alkaline oxides and borate, the mechanism of attack by acid and alkaline solutions on glass has to be fundamentally different. Water and acid solutions remove the alkaline oxides from the glass surface, leaving a protective layer of silica gel which makes glass resistant to further attack. Alkalis which form soluble silicates destroy the protective layers. Therefore, an alternating treatment of glassware with strong acids and alkalis, as is sometimes done in cell cleaning, causes a chemical stress least compatible with glass, and should be avoided. Although the attack of alkaline solutions on glass walls is impeded by the leaching out of ions, particularly the aluminum ion, its concentration has to be quite high, i.e., in the millimole range, making the ion a contaminant of the solution. The presence of a layer of silica gel on the surface of glassware makes it prone to adsorption of ions and gases.

By selecting an appropriate composition, the properties of glass can be changed over a wide range so that a glass material can be adopted for the purposes required in each particular case. For cell construction, the borosilicate glasses, especially Pyrex 7740 (or the corresponding Duran 50 glass of Jena), are the most commonly used as they combine good general chemical stability with good thermal shock resistance. However, Pyrex glasses contain in their constitution elements such as As which can make a very undesirable impurity in some studies. In such cases, special glass, free of the impurities, must be used, e.g., the As-free "Hysil" (a U.K. proprietary material), instead of Pyrex. When high purity of a nonalkaline solution is essential and the operations require heating or boiling, quartz is used as, e.g., for the last stage of a multiple-stage water distillation apparatus. For optical windows or whole optical cells requiring uv transmission, quartz or a variety of high-silica containing glasses (Vycor glasses) with general properties similar to quartz are used. Some of them have additional transparency in the near infrared. A boron-free glass, resistant to alkalis (Corning No. 7280) but having low resistance to thermal shock, is also available. For gas-tight high-temperature ovens, quartz or Vycor glasses having the highest softening temperature of all glasses are used.

To combine glasses with different coefficients of expansion, commercially available graded seals are used in which the coefficient of expansion of glass is gradually varied by changing the composition of the glass along the tube. The use of graded seals is restricted since the seals are rather brittle and cannot be subjected to elevated temperatures.

Glasses allowing a leak-free seal to metals are of great importance for construction of electrochemical apparatus. In order to assure a satisfactory seal, the glass must obviously have a coefficient of expansion similar to that of the metal and wet the surface of that metal. What is called "glass wetting the metal" is actually the glass reacting with the oxide layer which usually covers most metal surfaces. For a successful seal, the degree of oxidation of the metal is critical. Several glasses suitable for glass-to-metal seals are listed in Table 5.

4.2.2. Procedure for Cleaning of Glassware

Glass apparatus or other ancillary glassware, which is used for the first time, is best washed by soaking it for 24 h in fresh chromic-sulfuric solution (a CrO_3 -concentrated H_2SO_4 mixture), rinsing it thoroughly, and soaking it in good-quality distilled water for the same length of time as it was in chromic solution to remove chromium ions adsorbed on the walls. The apparatus thus cleaned is kept filled with concentrated H_2SO_4 during storage, and, before every run, washed again with fresh concentrated H_2SO_4 , hot concentrated H_2SO_4 , or, as some authors prefer, with a mixture of concentrated H_2SO_4 and HNO_3 or even with oleum. HCl and HNO_3 should, however, rather be avoided, because their volatile components make the rinsing out of the cleaning solution difficult and Cl^- ions may remain adsorbed. Careful, repetitive rinsing with distilled water of the highest purity and finally with the solution itself should be done in such a way as to prevent the glass walls becoming dry when in contact with air. The clean cell or flask is then filled with the test solution and closed in an airtight manner. In a clean cell or flask, no hydrophobic ring should develop on the glass walls at the water level, even after days of storage of high-purity water or solution in the vessel. After the run, and before concentrated H_2SO_4 is again put into the cell, all the solution and any precipitates, if formed in the cell, should be removed by suitable rinsing, or dissolved and rinsed out.

Table 5
Some Glass-to-Metal Seals

Metal	Glass
Pt	Soft glass, without lead, for electrode sealing
Pt	Pyrex 7740
W	Pyrex 7991, Uranium glass 3321
Cu	Pyrex
Fe	Potash-soda-lead
Kovar	Pyrex, Novex

For special systems, it may be necessary to age the glass surface first by leaching the glass with the electrolyte or hot water. When traces of adsorbed ions have to be removed from the glass surface, as in some studies, e.g., of surface oxide film processes which are sensitive to adsorption of SO_4^{2-} or Cl^- ions at levels of 10^{-6} – 10^{-8} M, boiling water of high purity is used.⁽⁴⁾ To minimize the possibility of contaminants entering from the air into the cell during the time of desorption of ions, these operations are best carried out in a plastic tent under N_2 .

4.2.3. *Materials Other than Glass for Cell Construction*

For work with substances which attack glasses, the electrochemical cell is usually made out of Teflon (TFE, polytetrafluoropolyethylene) which is inert chemically to all substances. Teflon is not thermoplastic nor can it be glued, so that an electrochemical cell made out of Teflon has to be assembled from individually machined parts. The Teflon parts retain their shape as long as they are not heated but even soaking in boiling water, which is sometimes done during cleaning procedures, may deform Teflon pieces to the extent that the individual parts of the cell may not fit together anymore. The rather loose texture of Teflon allows a strong ad(ab)sorption of ions or gases on/in its surfaces. This makes the selection of a cleaning solution for a Teflon cell rather difficult, specially since the extent of ad(ab)sorption of various substances has not yet been properly studied. Considering the chemically inert character of Teflon, any cleaning solution can be used. It is however, not easy to determine prior to an experiment if the cell is actually clean or not because Teflon is not wetted by water. The absence of wetting creates a danger of adherence of gas bubbles on, e.g., the tip of the Luggin capillary or in the tube between the working and counter electrode compartments. This will cause an interruption of the electrical circuit in the cell. The high absorption power, the absence of wetting by water solutions, and the lack of transparency makes work with Teflon cells rather difficult.

Kel-F (chlorofluoropolymer), which has also been used for fabrication of cells, is a material similar to Teflon, with better mechanical properties but not as chemically inert as Teflon.

Other polymers, e.g., PE (polyethylene), PS (polystyrene), or polysulfones are also sometimes used for cell construction because of their flexibility, transparency, of their ability to be thermally formed. Generally polyethylenes and polystyrenes are resistant to alkalis but are attacked slowly by oxidizing acids. Low density PE and PS are soluble in aromatic solvents, PS also in chlorinated hydrocarbons.

Some properties of the plastic materials used in construction of electrochemical cells are given in Table 6. As the properties of various materials, specially the chemical resistance, vary depending on the manufacture, the resistance of the materials used for cell construction should be verified with the manufacturer or checked in the laboratory.

Table 6
Some Properties of Plastic Materials

Material	TFE	PE		PS	PP	Acrylic	Nylon	PVC	PC
		high density	low density						
Temperature, °C max. of britleness Burning Transparency	275 -270 no opaque	120 -100 very slow translucent or opaque	95 -100 translucent or opaque	70 20 slow translucent or opaque	140 0 slow translucent or opaque	slow transparent	self-extinguishing translucent or opaque	60 -30 transparent or opaque	130 -135 transparent or opaque
Chemical resistance: to acids, weak strong oxidizing	+++	++ ++ attacked	+ +	+++ attacked	+ } attacked	+++ ++ attacked by conc.	+ } attacked	+++ ++ attacked by conc. HNO ₃	+ } attacked
to alkalis, weak strong	+++	++ ++	+ +	+++ +++	+++ ++	+++ attacked	+ +	+++ +++ attacked by conc.	attacked
Organic solvents	+++	+ below 80°C	soluble aromatic above 60°C	soluble in aromatic and chlorinated hydrocarbons	+ below 80°C soluble in ethers, benzene	soluble in ketones, esters, aromatic & chlorinated hydrocarbons	+ to most	soluble in ketones and esters resistivity depends on type	soluble in aromatic and chlorinated hydrocarbons, ketones and esters
Hydrogen peroxide	+++	+++			+++		attacked	attacked	attacked
+++ inert ++ very good + good	TFE—Teflon PE—polyethylene PS—polystyrene	PP—polypropylene PVC—polyvinylchloride PC—polycarbonate							

Very convenient for mounting electrodes and for connecting parts of an electrochemical cell or gas line are the heat-shrinkable tubings made in a choice of fluoropolymers. All types of shrinkable tubes are electrically insulating and non-flammable and most of them are chemically inert. They differ mainly in mechanical properties, transparency, and in the temperature required for shrinking and of working as can be seen from Table 7. A cell for electrochemical studies at high hydraulic processes was recently made from shrinkable⁽¹⁴⁹⁾ Teflon tubing, sealed to glass.

5. Gases

Gases which enter the cell working compartment during electrochemical measurements, usually to deoxygenate the solution or to provide better mass transport by stirring or sometimes as reagent, have to be rigorously purified in order not to contaminate the system. The methods of purification, elaborated in the fifties,⁽¹⁴⁾ are essentially the same today. In a typical gas line, a high-purity gas from a cylinder—hydrogen, nitrogen or noble gas—passes through a safety valve, then, to remove water, CO and hydrocarbons, through traps with MgClO_4 and molecular sieve (4A type), and is later deoxygenated in a furnace, with palladized asbestos at 450°C in the case of hydrogen, or with copper turnings or copper-coated silica gel at 350°C in the case of nitrogen or helium. Then, water and the last traces of impurities are removed in 2–3 traps with activated charcoal kept at liquid nitrogen temperature. Finally, before entering

Table 7
Properties of Shrinkable Tubing Materials

Material	Temperature (°C) of		Properties		
	Shrinking	Use	Chemical	Optical	Mechanical and other
TFE (Teflon)	330	290	Inert	—	Not too good impermeability
FEP ^a	180	200	High resistance	Transparent	Thermoformable, melting
TFE over FEP	330	200	Inert Less resistive	Transparent	Good mechanical, impermeable
PFA	190	260		Transparent	
E-TFE (Tefzal) ^b	150	190		Transparent	
E-CTFE (Halar) ^c	150	180			

^a Teflon FEP—fluorinated ethylene/propylene copolymer.

^b E-TFE—copolymer of ethylene and TFE.

^c E-CTFE—copolymer of ethylene and chlorotrifluoroethylene.

the cell, the gas is saturated with the solvent in a presaturator containing the test solution. All connections from the gas line to the cell are made by Teflon tubes.

Tank hydrogen can also be purified in an elegant method by letting it diffuse through heated Pd or palladium-silver tubes, but due to rather low flow rates and the danger of cracks, which can develop in the tube, the use of this method is restricted. High-purity hydrogen is sometimes obtained electrolytically on Ni electrodes from concentrated NaOH or on Pt electrodes from sulfuric acid solution.

From oxygen, organic impurities are removed by burning them in an oven at 800°C in the presence of a catalyst.

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3

Non-Steady State Techniques

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Introduction

A list of symbols used in this chapter with their definitions can be found on page 170.

The knowledge of elementary electrochemical processes has been considerably increased thanks to improvements in the techniques used for regulating the quantities which, in turn, regulate the state of the interface. In particular, it has been possible to perform a steady state investigation of more and more complicated systems. However, although such an investigation is sometimes sufficient in the case of simple processes to find the reaction mechanism and/or the kinetic parameters, it becomes clearly insufficient when the degree of complexity of the reactions involved and/or the couplings between the elementary processes become higher. In that case, it is necessary to use non-steady state techniques.

Use of these techniques rests on principles analogous to those which justify relaxation methods used at equilibrium in chemical kinetics. Disturbing the reaction from steady state by applying a perturbation to the electrochemical system allows the system to relax to a new steady state. As the various elementary processes (diffusion, adsorption, heterogeneous reactions, desorption, etc.) relax at different rates, the transient response can be analyzed to dissect the overall electrochemical process and to extract the desired kinetic information.

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Even if these techniques are often used only to get around the problem of mass transport so as to see fast kinetics and adsorption effects, it is now necessary to use them in order to study complex reaction mechanisms involving several intermediates.

The quantities employed most frequently to identify the processes governing the interface behavior are electric quantities for they are easy to handle and particularly rich in information. As the reaction rates of the heterogeneous reactions are often potential dependent, a perturbation of the potential of the electrode will give information about the electrochemical processes involved at the interface. In the same way, as the rate constants are strictly related to the current, a perturbation of the latter will provide the same type of information. However, other quantities can also be used as will be seen below (perturbation of the pressure, the electrode area, the rotation speed, the concentrations of the reactants, the temperature, *etc.*).

The principle of the measurement set-up, allowing the regulation and then the analysis of the processes at the interface on one hand and the elaboration of the models which are to be compared with the experimental data on the other, requires an accurate description of the kinetic and electric laws governing the interface. The choice of one technique among those surveyed in chapters 3 and 4 will depend on whether one is trying to establish a reaction mechanism, i.e., testing a model, or determining kinetic parameters of a known, or at least so assumed, mechanism. Some techniques are extensively used because they are well suited for extracting kinetic parameters when the mass transport is bothersome. In certain very favorable cases several techniques may be of comparable utility. However, when complex heterogeneous reactions interact with mass transport, time analysis of the transient will lead to very poor results in trying to extract a reaction mechanism and a frequency analysis (see next chapter) will be more efficient.

The present study is not, of course, an extensive investigation of non-steady state techniques, and therefore it might be fruitful for the reader to refer also to certain basic and classic publications on this topic.⁽¹⁻⁸⁾ The reader will find there all the details on the classical techniques (step, ramp techniques). Instead in this review only the main points are given because the new trends of the non-steady state techniques (convolution procedure, oscillation analysis, electrochemical noise measurements), which can hardly be found elsewhere, are emphasized.

1. Introduction to the Study of Electrochemical Systems in Terms of Non-Linear System (NLS) Analysis

1.1. Electrochemical Systems Considered as NLS

When an interface is perturbed from its equilibrium by means of an external energy source, a permanent flow of charge and matter appears. This

is only possible due to (i) the existence of electrochemical reactions allowing the electric charge transfer between the electrode (metallic or semiconductor) and the ionic conductor, and (ii) the gradients of electric and chemical potentials which make possible the transport of the reacting species between the bulk of the electrolyte and the reaction zone. The elementary laws which govern the kinetics of mass transport and those of the various electrochemical reactions, as well as the complex couplings between these two types of elementary processes, assign to the electrochemical system of interest a non-linear behavior which can often be very pronounced.

For example, it is well known that charge transfer generally obeys, at least approximately, an exponential activation law (Tafel's law) leading to a relationship between the faradaic current I_F and the overvoltage η ⁽⁹⁾ such as:

$$I_F = I_0 \exp \left(\frac{\alpha n F}{RT} \eta \right) \quad (1)$$

where α is the transfer coefficient, n the number of electrons implied in the transfer, F the Faraday constant ($=96,500$ C), R the molar gas constant, T the absolute temperature, and I_0 the exchange current.

Experimentally, there are many obvious examples of non-linear behavior. Various examples are shown in Figure 1: (i) an N-shaped current-potential curve recorded in the case of iron passivation in a neutral medium⁽¹⁰⁾; (ii) an S-shaped curve in the case of zinc electrocrystallization in a Leclanché-cell medium⁽¹¹⁾; (iii) a Z-shaped curve in the case of iron passivation in a molar sulfuric acid medium ($pH = 0$).⁽¹²⁾

1.2. Modeling of the Electrochemical System

The study of a physical phenomenon often leads to the elaboration of a model, that is to say that such a study is a mere identification problem.⁽¹³⁾ One looks for a model for a rational representation, often mathematical, of the phenomenon. This allows one first to account for all the facts observed experimentally, and secondly to predict the behavior of the system under other conditions. The model often deals with the very structure of the system, but, in certain cases, it can also be useful to elaborate a model of the "input-output" type (equivalent circuit for example), describing the behavior of the system with respect to its environment.

The aim of the electrochemist is generally to identify the processes occurring at the interface either by elaborating a model for the interface behavior, or by trying to find the value of some parameters of the system of interest when the reaction mechanism involved is already known.

The elaboration of a model for the interface behavior is derived from the general equations of physics that take account of the non-linear character of the processes involved. Comparison of the model with experimental data

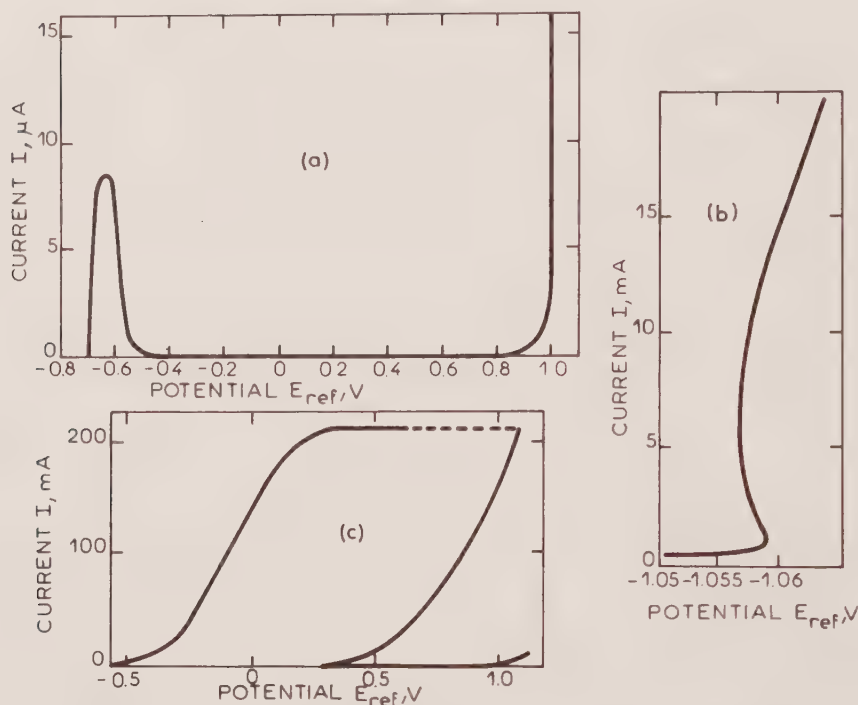


Figure 1. Some examples of polarization curves of electrochemical interfaces. (a) N-shaped anodic curve: iron electrode in basic medium, pH 8.42 (0.15 *N* boric acid and 0.15 *N* sodium borate) [from Reference (10)]; (b) S-shaped cathodic curve: zinc in Leclanché-cell electrolyte (0.72 *M* $ZnCl_2$ + 2.67 *M* NH_4Cl) [from Reference (11)]; (c) Z-shaped anodic curve: iron in sulfuric acid medium, pH 0 [from Reference (12)].

requires calculations which can be more or less complicated according to the complexity of the model to be tested. There are several ways of simplifying the calculations. One of the most interesting consists in linearizing the non-linear equations which describe the model.

1.3. Characterization of the Electrochemical System

Two different types of methods, based on the use of either large- or small-amplitude signals, can be utilized to characterize the electrochemical system theoretically and experimentally.

1.3.1. Large-amplitude Signal Analysis of NLS

This study is often difficult and generally requires a very time-consuming use of a computer to obtain the theoretical response of the model to be tested. It is necessary to consider each case as a particular case and take account of

the nature of the input signal applied to the system (current, charge, potential, for example, when electric quantities are used) and of its shape.⁽¹⁴⁾ Various signals are exemplified in Table 1.

1.3.2. Small-amplitude Signal Analysis of NLS

It can be shown that the behavior of a NLS can be described entirely if the behavior of the linear system obtained by linearizing the equations which describe the actual NLS is known at every point of the steady state characteristic.^(15,16) Thus, by analyzing the NLS locally the problem is reduced to the well-known field of linear systems theory.⁽¹⁷⁾

In the case of a linear system, the shape and nature of the input signal have no importance for they are equivalent to each other. Therefore, one has to define only one quantity from which all the behaviors of the linear system to be studied can be derived. This sole quantity—which can be the impulse response, the step response, a transfer function, or the impedance, etc.—allows a complete characterization of the linear system.

Let $h(t)$ be the impulse response of a linear system. If $x(t)$ and $y(t)$ are the input and output signals, respectively, then

$$y(t) = \int_{-\infty}^{+\infty} h(\theta)x(\theta - t) d\theta \quad (2)$$

whatever the shape of the input signal. For example:

(i) If $x(t)$ is a Dirac impulse $\delta(t)$ (i.e., white noise), the output signal is:

$$y(t) = \int_{-\infty}^{+\infty} h(\theta)\delta(\theta - t) d\theta \equiv h(t) \quad (3)$$

and defines the impulse response of the system.

(ii) If $x(t)$ is a step signal $\Gamma(t)$ [see Table 1(a)], the step response is:

$$y(t) = \int_{-\infty}^{+\infty} h(\theta)\Gamma(\theta - t) d\theta \quad (4)$$

Now $\Gamma(t) = 1$ for $t > 0$ and $\Gamma(t) = 0$ for $t < 0$ and hence

$$y(t) = \int_t^{\infty} h(\theta) d\theta \quad (5)$$

which defines the step response of the system.

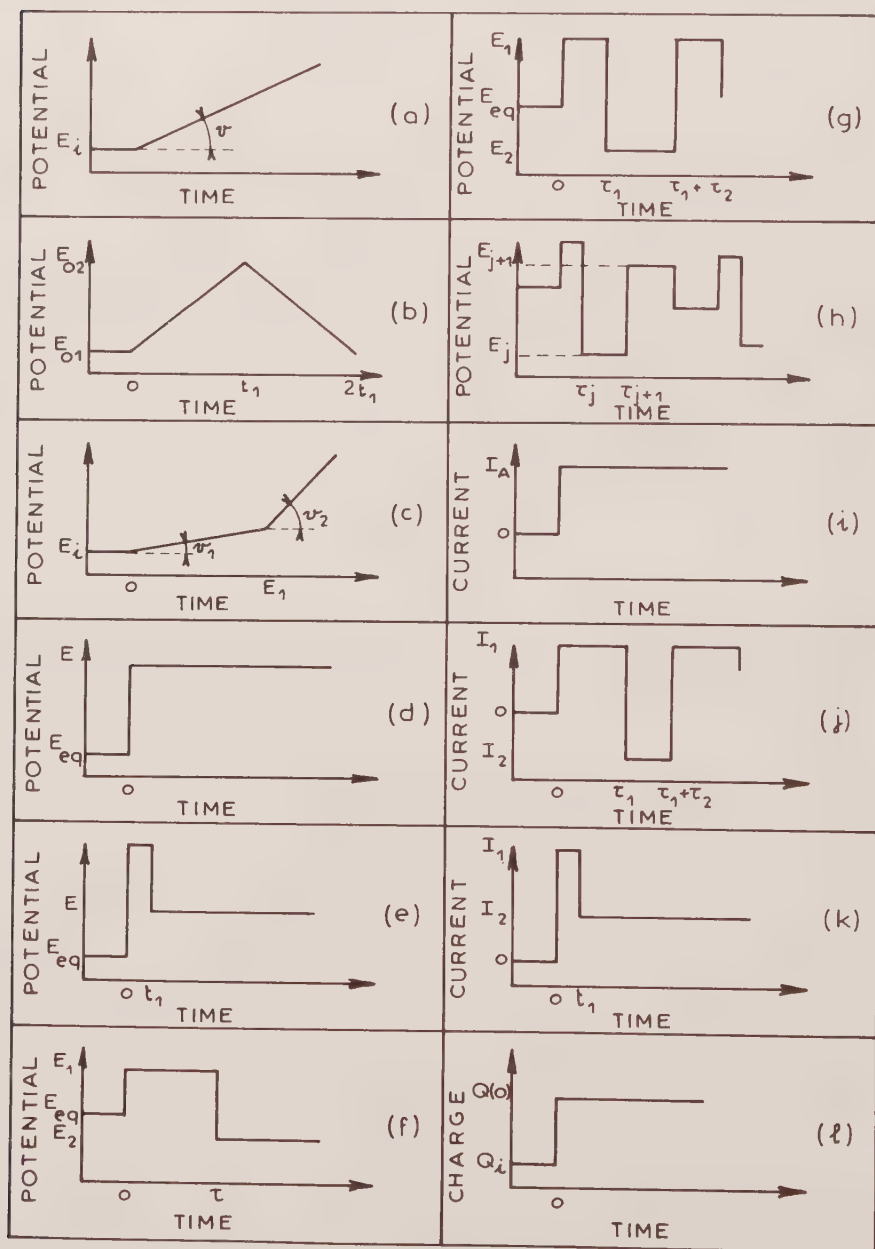
(iii) Making a Fourier transform of Eq. (2) we obtain:

$$Y(\omega) = H(\omega) \cdot X(\omega) \quad (6)$$

and

$$H(\omega) = \frac{Y(\omega)}{X(\omega)} \quad (7)$$

Table 1
Typical Signals Used in Relaxation Methods



where the transfer functions $H(\omega)$, $X(\omega)$, and $Y(\omega)$ are the Fourier transforms of $h(t)$, $x(t)$, and $y(t)$, respectively, and $\omega = 2\pi\nu$ (ν = frequency).

By imposing a sinusoidal input signal $X(\omega) = x_0 \exp(j\omega t)$, we obtain $H(\omega)$, frequency by frequency, which is either an impedance if X is a current and Y a potential (or an admittance if X is a potential and Y a current), or any transfer function. For example an electrohydrodynamical impedance is defined if X is the current and Y the rotation speed of a rotating disc electrode (see Section 5.5).

Thus, the behavior of an electrochemical interface can be characterized entirely if $h(t, E)$ [or $H(\omega, E)$] is known at every polarization point E of the current-potential curve.

1.4. General Considerations on the Analysis of Electrochemical Systems

We summarize below the way to proceed (which is represented schematically in Figure 2).

The electrochemist has available a system on which he wishes to test a certain model. Two distinct approaches are followed: one of them is experimental and leads to results presented as curves or tables, the other one is theoretical and leads to analytical expressions (or tables provided by a computer). In practice, the two approaches are not independent and the information drawn from one of them often allows the electrochemist to enhance the development of the other one. Furthermore, a certain "feedback" will allow, when comparing the theoretical and experimental results, readjustment of the model or even the conditions of the experiment.

This general analysis assumes no *a priori* knowledge, neither on the system studied nor on the model liable to explain its behavior. However, in many cases, the work is easier either because the appropriate model is already known

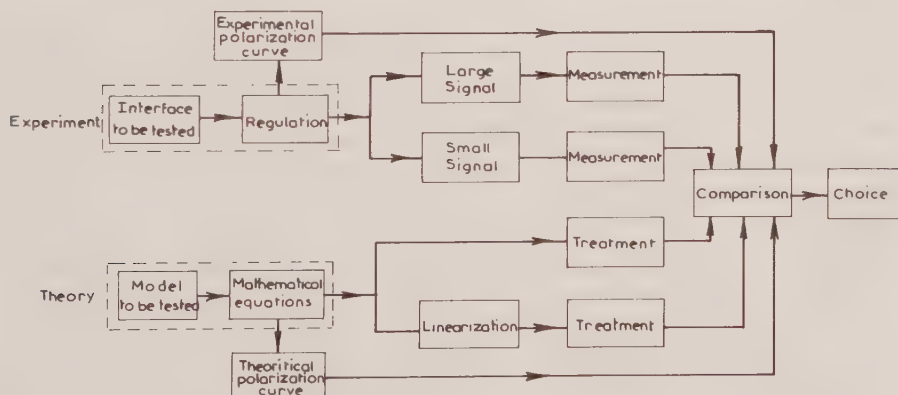


Figure 2. Synopsis of the study of an electrochemical interface.

and only certain parameters are to be studied, or because numerous models, and a simulation of their behavior, are available in the literature.

Before describing the techniques that can be used for analyzing the behavior of an electrochemical system, we shall present some general considerations relative to the models describing the interface and their mathematical treatment on the one hand, and to the measurement methods on the other.

2. General Concepts on Electrochemical Interfaces

2.1. General Considerations on the State Equations of the Interface

A classical dynamical system is defined by a certain number of quantities among which one can distinguish the input variables W (or constraints), the output variables Y (or observables) and the state variables X [$W = (w_1, w_2, \dots)$, $Y = (y_1, y_2, \dots)$, $X = (x_1, x_2, \dots)$ being vectors].⁽¹⁸⁾ For such a system, which is assumed to be causal, it is necessary and sufficient to know an initial state $X(t_0)$ and an input variable W in order to determine the state at any instant $t > t_0$.

$$X(t) = \mathcal{F}(t_0, t, X(t_0), W) \quad (8)$$

where $\mathcal{F}$ is the state transition function which describes the behavior of the system. This function $\mathcal{F}$ is the solution of a set of integral-differential equations subjected to boundary and initial conditions. Equation (8) is the law describing the behavior of the model considered.

The output quantity to be analyzed, Y , depends on the state of the system and therefore is a function such as, for example:

$$I(t) = \mathcal{G}(t_0, t, X(t_0), W) \quad (9)$$

if current I is chosen as an observable quantity.

Different types of approaches for analyzing the interface behavior theoretically have been proposed. The first of these approaches, based on classical thermodynamics, turned out to be very limited, since all the descriptions elaborated by generalizing the laws valid at equilibrium to out-of-equilibrium conditions are inadequate. On the contrary, the justification of equations describing the macroscopic behavior from the microscopic behavior of the system, i.e., by using statistical mechanics, has been shown to be very possible.⁽¹⁹⁾ This approach reveals that the state of the interface can be characterized by a set of internal quantities $E(M, t)$, $c_i(M, t)$, $T(M, t)$ which are the state variables (local instantaneous potential, concentration of species i , and temperature at point M and instant t , respectively).

The space distribution of the state variables is determined thanks to a set of integral-differential equations (Maxwell equations and mass balance

equations) subjected to appropriate boundary and initial conditions. If the propagation of the electric field is disregarded and if temperature is assumed to be uniformly distributed, then by averaging all the quantities the evolution law of the state variables is a solution of the system:

$$\nabla^2 E = -\rho_c + \nabla \mathbf{P} \quad (10)$$

$$\frac{\partial c_i}{\partial t} = -\nabla \mathbf{J}_i + \xi_i \quad 1 \leq i \leq m \quad (11)$$

Among these $(m + 1)$ coupled equations, the first one generalizes the Poisson equation where ρ_c is the electric charge density per unit volume and $\mathbf{P}$ the dielectric polarization. The following m equations generalize the hydrodynamic equations and apply to the m types of chemical entities involved in the system; c_i is either a surface or a bulk concentration; $\mathbf{J}_i$ is the flux and ξ_i is a term representing the sources (production and consumption) of the entities i generally arising from chemical and electrochemical reactions. This term can be made explicit from the mass balances of the reaction scheme to be tested and from the laws of homogeneous or heterogeneous kinetics.

The input variables (or constraints) can be considered as being of two quite different sorts:

a) the external quantities imposed by the experimenter and by the environment, which constitute the experimental conditions. These control quantities are introduced in the model by the boundary and initial conditions of the differential equations. Thus, vector $\mathbf{W}$ can be formed by:

c_i^* : concentration of species i in the bulk of the solution.

E_{ref} : potential difference between the reference electrode and the working electrode.

T : absolute temperature.

P : pressure.

A : area of the electrode.

Ω : rotation speed of the electrode.

b) the internal quantities, ℓ_i , called noise sources, which perturb the system and cannot be controlled by the experimenter.

Therefore, the current I is a function G such as:

$$I = \mathcal{G}[t_0, t, X(t_0), \ell_i, c_i^*, E_{\text{ref}}, T, P, A, \Omega] \quad (12)$$

The last six quantities, which can play the role of experimental control quantities, enable the experimenter to act on the state of the system and hence on the output variables. They allow a classification of the investigation methods. For example, the methods where E_{ref} or I are varied and analyzed, whereas c_i^* , T , P , A , and Ω are maintained constant, are classified as electric techniques. But, all the other quantities can be used as control quantities thus constituting other types of techniques for analysing electrochemical systems.

2.2. General Considerations on Interface Models

Starting from the general framework defined above, the elaboration of a model for the interface will be performed by making a certain number of hypotheses which generally allow one to simplify the initial Eqs. (10) and (11). These simplifying hypotheses fall into several categories which will be briefly described below.

2.2.1. The Poisson Equation

It is often assumed that the Laplace equation is a good approximation of the Poisson equation:

$$\nabla^2 E = 0 \quad (13)$$

This is valid at every point of the solution bulk as a result of electro-neutrality, except in the double-layer.⁽²⁰⁾ The influence of radial gradients has been studied by Newman⁽²¹⁾ who calculated the current distribution at the electrode surface, but one generally considers only the transverse potential gradient. This leads to the idea that the ohmic drop due to the electrolyte resistance is added to the potential difference across the interface.

2.2.2. Separation of the Faradaic Current from the Charging Current of the Double-Layer

Strictly speaking, there is a close coupling between the faradaic current I_F and the charging current I_C of the double layer,⁽²²⁾ but in most models it is assumed that they can be separated. Then the overall current I is:

$$I = I_F + I_C \quad (14)$$

and the interface can be schematized in the case of small perturbations by the equivalent circuit shown in Figure 3, where the double-layer behavior is represented by a capacity C_d .

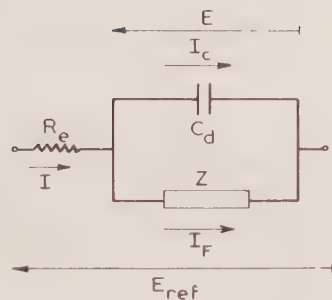
2.2.3. Equations Describing the Concentration Change

The hypothesis often made is that of a dilute solution for which the flux of a species i can be separated into a flux due to diffusion and a flux due to migration in an electric field.⁽²³⁾ In this case, the equation giving the concentration change is, in the absence of a chemical reaction (otherwise ξ_i has to be added):

$$\frac{\partial c_i}{\partial t} = \nabla(D_i \nabla c_i) - \mathbf{v} \cdot \nabla c_i + F n_i \nabla(\mu_i c_i \nabla E) \quad (15)$$

where $\mathbf{v}$ is the velocity of the liquid; D_i the diffusion coefficient of species i ; μ_i the mobility of i ; n_i the charge number of i ; and E the electric potential.

Figure 3. Equivalent circuit of an electrochemical interface. R_e : electrolyte resistance; C_d : double-layer capacity; $Z(\omega)$ is related to faradaic processes; E is the potential difference applied across the interface; and E_{ref} the potential difference imposed by a potentiostat between a reference electrode and a working electrode.



Thus the concentration is modified under the simultaneous influence of diffusion (first term), convection (second term), and migration (third term).

Assuming that the transport properties (D_i , μ_i) are uniform in the solution bulk, and hence are independent of c_i , one can write:

$$\frac{\partial c_i}{\partial t} = D_i \nabla^2 c_i - \mathbf{v} \nabla c_i + F n_i \mu_i \nabla (c_i \nabla E) \quad (16)$$

If the electroneutrality of the solution is assured, in the presence of major ionic species which are assumed not to take part in the reaction (supporting electrolyte), one can neglect the migration term. Generally calculation of concentration in the presence of convection is difficult unless very particular hydrodynamic conditions are fulfilled. The most famous case of the rotating disk electrode gives rise to a constant concentration gradient at the electrode [uniformly accessible electrode⁽²³⁾]. However, in other cases, calculation of concentration is simple only if one can disregard convection. This happens when Schmidt's number ν/D_i (ν is the kinematic viscosity) is sufficiently high (several thousands). The concentration gradient is then located in a layer, called the Nernst layer, of thickness δ_N , within which the liquid is nearly motionless ($\mathbf{v} = 0$). The transport equation can then be reduced to Fick's equation with good accuracy:

$$\frac{\partial c_i}{\partial t} = D_i \nabla^2 c_i \quad (17)$$

Convection is implicitly taken into account by applying the boundary conditions on c_i , that is $c_i = c_i^*$, at a finite distance δ_N from the electrode surface. If the assumption that the diffusion layer has an infinite thickness is made in integrating Eq. (17), the solutions obtained may not be satisfactory at long times (or at low frequencies).

2.2.4. Heterogeneous Reactions at the Interface

In applying the laws of heterogeneous chemical kinetics to the adsorbed species involved in the electrochemical kinetics, we can write the mass-balance

equation for a species i :

$$\frac{\partial c_{Si}}{\partial t} = \xi_i + D_{Si} - \nabla^2 c_{Si} \quad (18)$$

where ξ_i , the source term, can be either positive or negative and represents here the electrochemical or chemical surface reactions, the adsorption, or the desorption; D_{Si} is the surface diffusion coefficient of species i . The surface concentration c_{Si} is generally considered as being proportional to the fractional coverage θ_i of the electrode surface

$$c_{Si} = \beta_i \theta_i \quad (19)$$

where β_i is the maximum surface concentration of species i .

By analogy with gas phase adsorption, in order to express the value of θ_i one chooses an isotherm law expressing the occupation of the surface, the interactions between adsorbed species, and the distribution of adsorption energy between the various sites. The shape of the isotherm chosen has a considerable influence on the laws relating the reaction rate to the potential and the bulk concentration of the species. The most commonly adopted isotherm law is the Langmuir isotherm.^(24,25)

2.2.5. Linearized Form of the State Equations⁽¹⁷⁾

The state variables ($E, c_1, c_2, \dots, \theta_1, \theta_2, \dots$) form the vector X which obeys equations of the type

$$dX/dt = f(X, W) \quad (20)$$

The observation equation is:

$$Y = g(X, W) \quad (21)$$

Linearizing Eqs. (20) and (21) leads to relationships between small variations ΔX , ΔY , and ΔW of X , Y and W , respectively:

$$\frac{d\Delta X}{dt} = \left(\frac{\partial f}{\partial X} \right) \Delta X + \left(\frac{\partial f}{\partial W} \right) \Delta W \quad (22)$$

and

$$\Delta Y = \left(\frac{\partial g}{\partial X} \right) \Delta X + \left(\frac{\partial g}{\partial W} \right) \Delta W \quad (23)$$

If one sets $(\partial f / \partial X) = \mathcal{A}$ (state matrix); $(\partial f / \partial W) = \mathcal{B}$ (control matrix); $(\partial g / \partial X) = \mathcal{C}$ (observation matrix); and $(\partial g / \partial W) = \mathcal{E}$, then the canonical form of the linearized state equations is:

$$\frac{d\Delta X}{dt} = \mathcal{A} \Delta X + \mathcal{B} \Delta W \quad (24)$$

$$\Delta Y = \mathcal{C} \Delta X + \mathcal{E} \Delta W \quad (25)$$

If the stochastic behavior of the interface is considered, the noise terms ℓ_i which form the vector $\mathbf{l}$ must be introduced in Eq. (24), hence⁽²⁶⁾

$$\frac{d\Delta X}{dt} = \mathcal{A}\Delta X + \mathcal{B}\Delta W + \mathbf{l} \quad (26)$$

We shall see below how the noise terms ℓ_i are related to the fluctuations of the elementary processes.

In the next paragraph will be shown some examples of how the various hypotheses which have been described here can be applied.

2.3. Methods for Solving the State Equations

In illustrating the various methods of solving the state equations we shall consider the case where a reversible charge transfer is controlled by mass transport. In this case, the only reaction taking place at the interface is the redox reaction:



The concentrations c_R and c_O of species *Red* and *Ox* which diffuse from and towards the solution bulk are ruled by the following equations (known as Fick's second law) which are deduced from Eq. (17):

$$\frac{\partial c_O}{\partial t} = D_O \frac{\partial^2 c_O}{\partial z^2} \quad (28)$$

$$\frac{\partial c_R}{\partial t} = D_R \frac{\partial^2 c_R}{\partial z^2} \quad (29)$$

If species *Ox* and *Red* are assumed to diffuse linearly in the direction z perpendicular to the electrode surface, with coefficients D_O and D_R then the following initial and boundary conditions may be imposed:

- (i) initial conditions: the solution is homogeneous before the current flows

$$t = 0; z \geq 0: \quad c_O(z, 0) = c_O^*; \quad c_R(z, 0) = c_R^*$$

- (ii) boundary conditions at an infinite distance from the electrode

$$t \geq 0; z \rightarrow \infty: \quad c_O(z, t) \rightarrow c_O^*; \quad c_R(z, t) \rightarrow c_R^*$$

- (iii) boundary conditions at the electrode surface: since there is no adsorption, the fluxes of *Ox* and *Red* are the same and equal to the faradaic current because of mass and charge balance (known as Fick's first law).

$$t \geq 0; z = 0: \quad D_O \frac{\partial c_O}{\partial z}(0, t) = -D_R \frac{\partial c_R}{\partial z}(0, t) = \frac{I_F(t)}{nFA} \quad (30)$$

In addition, the current I_F is given by the heterogeneous kinetic law:

$$I_F(t) = nFA[(k_f c_O(0, t) - k_b c_R(0, t))] \quad (31)$$

where the surface concentration is assumed equal to the bulk concentration of the species near the surface ($z = 0$).

In Eq. (31):

$$\begin{aligned} k_f &= k_f^\circ \exp(-\alpha nFE/RT) \\ k_b &= k_b^\circ \exp[(1 - \alpha)nFE/RT] \end{aligned} \quad (32)$$

where k_f° and k_b° are constants independent of E .

At the standard (or normal) electrode potential E° , the rate constants of the forward reaction (k_f) and the backward reaction (k_b) will be equal. Hence:

$$k_f^\circ \exp(-\alpha nFE^\circ/RT) = k_b^\circ \exp[(1 - \alpha)nFE^\circ/RT] = k_s \quad (33)$$

and therefore

$$\begin{aligned} I_F &= nFAk_s \left\{ c_O(0, t) \exp \left[\frac{-\alpha nF(E - E^\circ)}{RT} \right] \right. \\ &\quad \left. - c_R(0, t) \exp \left[\frac{(1 - \alpha)nF(E - E^\circ)}{RT} \right] \right\} \end{aligned} \quad (34)$$

and

$$E^\circ = \frac{RT}{nF} \ln \frac{k_f^\circ}{k_b^\circ} \quad (35)$$

At the equilibrium potential E_{eq} where the electrode is at rest, the overall faradaic current is zero ($I_F = 0$) and the apparent exchange current I_0 is such that:

$$\frac{I_0}{nFA} = k_f c_O(0, t) = k_b c_R(0, t) \quad (36)$$

In this case, there is no concentration gradient at the electrode surface:

$$I_F = nFAD_O \frac{\partial c_O}{\partial z}(0, t) = -nFAD_R \frac{\partial c_R}{\partial z}(0, t) = 0 \quad (37)$$

and hence

$$c_O(0, t) = c_O^* \quad \text{and} \quad c_R(0, t) = c_R^* \quad \text{at } E = E_{eq} \quad (38)$$

and

$$I_0 = nFAk_f^\circ c_O^* \exp(-\alpha nFE_{eq}/RT) = nFAk_b^\circ c_R^* \exp[(1 - \alpha)nFE_{eq}/RT] \quad (39)$$

Consequently

$$E_{\text{eq}} = \frac{RT}{nF} \left(\ln \frac{k_f^\circ}{k_b^\circ} + \ln \frac{c_0^*}{c_R^*} \right) \quad (40)$$

$$E_{\text{eq}} = E^\circ + \frac{RT}{nF} \ln \frac{c_0^*}{c_R^*} \quad (41)$$

By dividing Eq. (31) by Eq. (40), one obtains:

$$I = I_0 \left\{ \frac{c_O}{c_O^*} \exp \left[-\frac{\alpha nF(E - E_{\text{eq}})}{RT} \right] - \frac{c_R}{c_R^*} \exp \left[\frac{(1 - \alpha)nF(E - E_{\text{eq}})}{RT} \right] \right\} \quad (42)$$

In opposition to k_s , the exchange current alone cannot characterize the electrochemical reaction kinetics because it depends on the concentrations of the reacting species.

For an ideally reversible system the rate constants k_f and k_b , as well as the exchange current I_0 , can be considered as infinitely high. Therefore, if charge transfer is assumed to be sufficiently fast with respect to diffusion, in order to remain under the conditions for a virtual or quasi-equilibrium at the electrode surface, then the boundary conditions at the electrode surface will be given by the Nernst equation instead of Eq. (30), i.e.,

$$\frac{c_O(0, t)}{c_R(0, t)} = \exp \left[\frac{nF}{RT} (E - E^\circ) \right] \quad (43)$$

However, one has to be careful when applying this relation to out-of-equilibrium conditions because it is actually valid only at equilibrium or for ideally reversible systems.^(27,28)

2.3.1. The Laplace Transform Method

The Laplace transform of $c(z, t)$ with respect to t is defined by

$$\mathcal{L}c(z, s) = \int_0^\infty \exp(-st) c(z, t) dt \quad \text{with } s = \sigma + j\omega \quad (44)$$

In applying the well-known properties of the Laplace transform to Eqs. (28) and (29), one can write that:

$$s\mathcal{L}c_i(z, s) - c_i(z, 0) = D_i(\partial^2 \mathcal{L}c_i(z, s)/\partial z^2) \quad (45)$$

where i denotes either the species *Ox* or *Red*, and, using the initial conditions:

$$s\mathcal{L}c_i(z, s) - c_i^* = D_i(\partial^2 \mathcal{L}c_i(z, s)/\partial z^2) \quad (46)$$

Since the solution of this second-order differential equation (of the form $d^2y/dz^2 - sy = k$) is the sum of a particular solution and the general solution of the equation without the right-hand member, the expression of $\mathcal{L}c_i(z, s)$ is:

$$\mathcal{L}c_i(z, s) = A_i \exp[-(s/D_i)^{1/2}z] + B_i \exp[(s/D_i)^{1/2}z] + (c_i^*/s) \quad (47)$$

The integration constants A_i and B_i are calculated using the boundary conditions. The boundary conditions at infinite distance lead to $B_i = 0$ and to the solution:

$$\mathcal{L}c_i(z, s) = A_i \exp[-(s/D_i)^{1/2}z] + (c_i^*/s) \quad (48)$$

hence

$$\mathcal{L}c_i(0, s) = A_i + (c_i^*/s) \quad (49)$$

The integration constant A_i depends on the boundary conditions at the electrode surface, and therefore on the constraint imposed. This will be exemplified in the case of two potentiostatic constraints.

2.3.1.1. Potentiostatic Step of Amplitude $\eta = E - E_{eq}$ [Table 1(d)]

Since k_f and k_b are constant at positive times, the current passing through the electrode surface is by Eqs. (31) and (49):

$$\frac{\mathcal{L}I_F}{nFA} = k_f \left(A_O + \frac{c_O^*}{s} \right) - k_b \left(A_R + \frac{c_R^*}{s} \right) \quad (50)$$

Now, by Eqs. (48) and (30),

$$D_O \frac{\partial \mathcal{L}c_O(0, s)}{\partial z} = -D_O A_O (s/D_O)^{1/2} = D_R A_R (s/D_R)^{1/2} \quad (51)$$

hence

$$-D_O^{1/2} A_O = D_R^{1/2} A_R \quad (52)$$

and

$$\frac{\mathcal{L}I_F}{nFA} = \left[k_f + k_b \left(\frac{D_O}{D_R} \right)^{1/2} \right] A_O + \frac{1}{s} (k_f c_O^* - k_b c_R^*) \quad (53)$$

and by Eq. (30)

$$\frac{\mathcal{L}I_F}{nFA} = -D_O^{1/2} A_O s^{1/2} \quad (54)$$

Consequently

$$A_O = -\frac{k_f c_O^* - k_b c_R^*}{s[k_f + k_b (D_O/D_R)^{1/2} + (D_O s)^{1/2}]} \quad (55)$$

Substituting into Eq. (54) results in:

$$\frac{\mathcal{L}I_F}{nFA} = \frac{k_f c_O^* - k_b c_R^*}{s[k_f + k_b (D_O/D_R)^{1/2} + (D_O s)^{1/2}]} (D_O s)^{1/2} \quad (56)$$

and hence

$$\mathcal{L}I_F = nFA(k_f c_O^* - k_b c_R^*)/s^{1/2}[\lambda + (s)^{1/2}] \quad (57)$$

with

$$\lambda = k_f/D_O^{1/2} + k_b/D_R^{1/2} \quad (58)$$

Consequently, by taking the inverse Laplace transform from a Table, one has

$$I_F(t) = nFA(k_f c_O^* - k_b c_R^*) \operatorname{erfc}(\lambda/t^{1/2}) \exp(\lambda^2 t) \quad (59)$$

with

$$\operatorname{erfc} z = 1 - (2/\pi^{1/2}) \int_0^z \exp(-z^2) dz \quad (60)$$

2.3.1.2. Time-dependent Potentiostatic Variation $E(t)$

In this case, Eq. (54) still holds. Since the Laplace transform of the current imposing the boundary condition cannot here be obtained directly, one has:

$$A_O = -\frac{\mathcal{L}I_F(s)}{nFA(D_O s)^{1/2}} \quad \text{and} \quad A_R = \frac{\mathcal{L}I_F(s)}{nFA(D_R s)^{1/2}} \quad (61)$$

Consequently, in combining Eq. (61) with Eq. (49), one obtains:

$$\mathcal{L}c_O(0, s) = -\frac{I_F(s)}{nFA(D_O s)^{1/2}} + \frac{c_O^*}{s} \quad \text{and} \quad \mathcal{L}c_R(0, s) = \frac{\mathcal{L}I_F(s)}{nFA(D_R s)^{1/2}} + \frac{c_R}{s} \quad (62)$$

As the inverse Laplace transform of A_i is given by the convolution product of the inverse Laplace transforms of $\mathcal{L}I_F(s)$ and of $1/s^{1/2}$, i.e., $I(t)$ and $1/(\pi t)^{1/2}$, respectively, Eq. (62) leads to

$$c_O(0, t) = c_O^* - \frac{1}{nFA(D_O \pi)^{1/2}} \int_0^t \frac{I_F(\theta) d\theta}{(t-\theta)^{1/2}} \quad (63)$$

and

$$c_R(0, t) = c_R^* + \frac{1}{nFA(D_R \pi)^{1/2}} \int_0^t \frac{I_F(\theta) d\theta}{(t-\theta)^{1/2}} \quad (64)$$

The general relation accounting for the concentration can be obtained as:

$$[c_O(0, t) - c_O^*]D_O^{1/2} + [c_R(0, t) - c_R^*]D_R^{1/2} = 0 \quad (65)$$

The only remaining thing to do is to substitute these values of $c_O(0, t)$ and $c_R(0, t)$ into the boundary conditions imposed by the faradaic current [Eq. (31) or (43)].

For example, instead of considering Eq. (31), it can be assumed that the Nernst equation [Eq. (43)] can apply at the electrode surface, and that there are no reducing species in the solution ($c_R^* = 0$) when the experiment starts.

In this case:

$$c_O^* - \frac{1}{nFA(D_O\pi)^{1/2}} \int_0^t \frac{I_F(\theta) d\theta}{(t-\theta)^{1/2}} = \left[\frac{1}{nFA(D_R\pi)^{1/2}} \int_0^t \frac{I_F(\theta) d\theta}{(t-\theta)^{1/2}} \right] \exp \left[\frac{nF}{RT} (E(t) - E^0) \right] \quad (66)$$

hence

$$\int_0^t \frac{I_F(\theta) d\theta}{(t-\theta)^{1/2}} = \frac{nFAc_O^*(D_O\pi)^{1/2}}{1 + (D_O/D_R) \exp [(nF/RT)(E(t) - E^0)]} \quad (67)$$

The integral equation thus obtained will be integrable or not according to the form of the $E(t)$ imposed. Let us note that Eqs. (63) and (64) are the base of the convolution (or semi-integral) procedure which will be applied in the following examples.

2.3.2. The Linearization Method: Examples of Electrochemical Impedances

Supposing a small potential perturbation $\Delta E \exp(j\omega t)$ is applied to the system, the corresponding current change $\Delta I_F \exp(j\omega t)$ is obtained by differentiating Eq. (31), and substituting the result in Eq. (28), and Eq. (29); after eliminating the $\exp(j\omega t)$ terms one has:

$$\frac{\Delta I_F}{nFA} = \frac{-\alpha nF}{RT} k_f c_O(0) \Delta E + k_f \Delta c_O(0) + \frac{(1-\alpha)nF}{RT} k_b c_R(0) \Delta E - k_b \Delta c_R(0) \quad (68)$$

$$j\omega \Delta c_i(z) = D_i \frac{\partial^2 \Delta c_i(z)}{dz^2} \quad (69)$$

where Δc_i (either Δc_O or Δc_R) is a small variation of c_i (either c_O or c_R) and $c_i(z, t)$ is such that $c_i(z, t) = \bar{c}_i(z) + \Delta c_i(z) \exp(j\omega t)$, where $\bar{c}_i(z)$ is the concentration of species i for d.c. polarization. Equations (68) and (69) lead to two important concepts: the charge-transfer resistance and the Warburg impedance.

2.3.2.1. The Charge Transfer Resistance R_{ct}

The charge transfer resistance defined by:

$$1/R_{ct} = (\partial I_F / \partial E)_{c_i = c_{te}} \quad (70)$$

becomes by virtue of Eq. (68):

$$1/R_{ct} = (nF/RT)[- \alpha k_f \bar{c}_O + (1-\alpha) k_b \bar{c}_R] nFA \quad (71)$$

This value generalizes, under non-equilibrium conditions, the concept of charge transfer resistance at equilibrium.⁽⁹⁾ As a matter of fact, under equilibrium

conditions, one has Eq. (39) and by substituting these values in Eq. (71) the well-known value of R_{ct} is found again:

$$R_{ct} = (RT/nF)(1/I_0) \quad (72)$$

Thus, for an ideally reversible process, since I_0 is infinitely high, R_{ct} tends to zero.

2.3.2.2. The Warburg Impedance

The resulting concentration perturbation $\Delta c_i(0, t)$ is obtained from the general solution of Eq. (69), i.e., from the following equation obtained after eliminating the $\exp(j\omega t)$ terms:

$$\Delta c_i(z) = M \exp[z(j\omega/D_i)^{1/2}] + N \exp[-z(j\omega/D_i)^{1/2}] \quad (73)$$

The integration constants M and N can be calculated from the boundary conditions, as follows:

(a) if the diffusion layer is assumed to be of infinite thickness, then $M = 0$ and hence:

$$\Delta c_i(z) = N \exp[-z(j\omega/D_i)^{1/2}] \quad (74)$$

and by Eq. (30)

$$\Delta I_F(t) = -NnFAD_O(j\omega/D_O)^{1/2} \exp(j\omega t) = NnFAD_R(j\omega/D_R)^{1/2} \exp(j\omega t) \quad (75)$$

After eliminating the integration constant N , one finds:

$$\frac{\Delta c_i(0, t)}{\Delta I_F(t)} = -\frac{1}{nFA(j\omega D_O)^{1/2}} \quad (76)$$

$$\frac{\Delta c_R(0, t)}{\Delta I_F(t)} = \frac{1}{nFA(j\omega D_R)^{1/2}} \quad (77)$$

Combining Eqs. (76), (77), and (68), one has

$$\Delta I_F = \frac{1}{R_{ct}} \Delta E - \left(\frac{k_f}{D_O^{1/2}} + \frac{k_b}{D_R^{1/2}} \right) \cdot \frac{\Delta I_F}{(j\omega)^{1/2}} \quad (78)$$

Hence by Eq. (57), one obtains for the impedance

$$Z(\omega) = \frac{\Delta E}{\Delta I_F} = R_{ct} \left[1 + \frac{\lambda}{(j\omega)^{1/2}} \right] \quad (79)$$

In Eq. (79), $R_{ct}\lambda/(j\omega)^{1/2}$ is usually called the Warburg impedance.⁽⁹⁾ $Z(\omega)$ is sketched in Figure 4a. It can be seen that the high-frequency limit of $Z(\omega)$ is equal to R_{ct} .

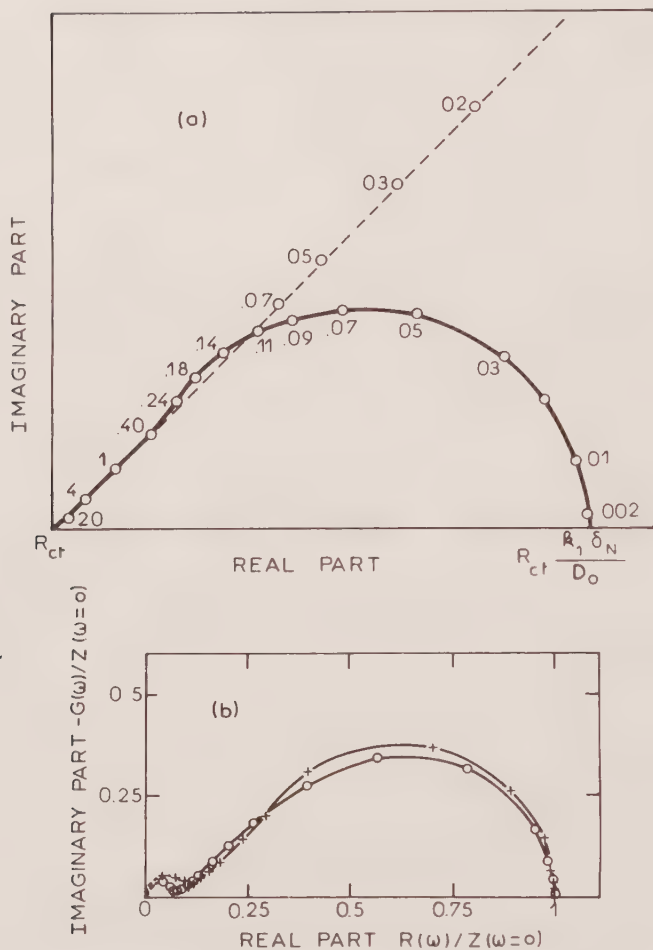


Figure 4. Simulated impedances in the case of diffusion. (a) Complex plane locus of the impedance for a reversible redox reaction in the case of only one species diffusing in the solution. Numbers on the curves indicate the frequency in kHz. Dashed line: (Warburg impedance) diffusion layer of infinite thickness. Solid line: diffusion layer of finite thickness δ_N (from Reference (29)). (b) Impedance simulated from Eq. (86) in the case of: (+) one diffusing species, (o) two diffusing species ($\delta_{N_O}^2/D_O = 1$; $\delta_{N_R}^2/D_R = 5$).

(b) if the diffusion layer is assumed to be of finite thickness and if the Nernst hypothesis is considered, i.e.,

$$c_i(z, t) = \begin{cases} c_i(0, t) + (c_i^* - c_i(0, t)) \frac{z}{\delta_N} & \text{for } z < \delta_N \\ c_i^* & \text{for } z \geq \delta_N \end{cases} \quad (80)$$

where δ_N is the thickness of the Nernst diffusion layer. Then by using the boundary conditions at $z = \delta_N$, the following equations can be obtained from

Eq. (73):

$$\Delta c_i(z) = \begin{cases} -2N \exp[-\delta_N(j\omega/D_i)^{1/2}] \sinh[(z - \delta_N)(j\omega/D_i)^{1/2}] & \text{for } z < \delta_N \\ 0 & \text{for } z \geq \delta_N \end{cases} \quad (81)$$

Thus by Eq. (30)

$$\Delta I_F(t) =$$

$$\begin{cases} -2NnFAD_O \exp[-\delta_N(j\omega/D_O)^{1/2}] \cosh \delta_N(j\omega/D_O)^{1/2} \cdot \exp(j\omega t) \times \sqrt{j\omega/D_O} \\ 2NnFAD_R \exp[-\delta_N(j\omega/D_R)^{1/2}] \cosh \delta_N(j\omega/D_R)^{1/2} \cdot \exp(j\omega t) \times \sqrt{j\omega/D_R} \end{cases} \quad (82)$$

and hence

$$\frac{\Delta c_O(0, t)}{\Delta I_F(t)} = -\frac{1}{nFAD_O} \cdot \frac{\tanh[\delta_N(j\omega/D_O)^{1/2}]}{(j\omega/D_O)^{1/2}} = -\frac{1}{nFA} N_O(\omega) \quad (83)$$

$$\frac{\Delta c_R(0, t)}{\Delta I_F(t)} = \frac{1}{nFAD_R} \cdot \frac{\tanh[\delta_N(j\omega/D_R)^{1/2}]}{(j\omega/D_R)^{1/2}} = \frac{1}{nFA} N_R(\omega) \quad (84)$$

Substituting Eqs. (83) and (84) into Eq. (68), one obtains:

$$\Delta I_F = \frac{1}{R_{ct}} \Delta E - \left[\frac{k_f}{D_O^{1/2}} \tanh \delta_N(j\omega/D_O)^{1/2} + \frac{k_b}{D_R^{1/2}} \tanh \delta_N(j\omega/D_R)^{1/2} \right] \frac{\Delta I_F}{(j\omega)^{1/2}} \quad (85)$$

Hence, in this case

$$Z(\omega) = R_{ct} \left[1 + \frac{k_f \tanh \delta_N(j\omega/D_O)^{1/2}}{(D_O j\omega)^{1/2}} + \frac{k_b \tanh \delta_N(j\omega/D_R)^{1/2}}{(D_R j\omega)^{1/2}} \right] \quad (86)$$

This impedance is sketched in Figure 4a. It should be noted that

- (i) if $\delta_N \rightarrow \infty$ we obviously find again the Warburg impedance
- (ii) if $\omega \rightarrow \infty$, as $\tanh \delta_N(j\omega/D)^{1/2}/(j\omega/D)^{1/2}$ is equivalent to $1/(j\omega/D)^{1/2}$, we find again the behavior of the Warburg impedance at high frequencies.

In Figure 4a the oscillation above the Warburg straight line (at frequencies between 0.4 and 0.14 kHz) is related to the convective effects. Numerical calculation taking account of the convection term in Eq. (17) has shown that the curve representing the impedance, in the case of control by both reaction and diffusion, is below the Warburg impedance.⁽³⁰⁾ Figure 4b shows the influence of the diffusion of the two species *Ox* and *Red* on the impedance diagram.

2.3.2.3. Impedances in the Case of Heterogeneous Reactions

In the case of multistep reactions at the electrode surface, the linearization method can be of great utility. For example, if we assume that species A

arrives at the surface by diffusion, adsorbs, and reacts at the electrode surface giving species B in two reaction steps according to the scheme:



where $k_i = k_i^\circ \exp(b_i E)$ and θ is the fractional surface coverage of the surface by species X^- , and if $c_B^*(0, t) = c_B$, then:

$$\beta \frac{d\theta}{dt} = k_1 c_B (1 - \theta) - k_2 \theta \quad (88)$$

$$I_F = FA[k_1 c_B (1 - \theta) + k_2 \theta] \quad (89)$$

For small variations $\Delta\theta$, ΔE , Δc_B , and ΔI_F of θ , E , c_B , and I_F one has:

$$j\omega\beta\Delta\theta = [b_1 k_1 (1 - \theta) c_B - b_2 k_2 \theta] \Delta E - (k_1 c_B - k_2) \Delta\theta + k_1 (1 - \theta) \Delta c_B \quad (90)$$

$$\Delta I_F = FA[b_1 k_1 (1 - \theta) c_B + b_2 k_2 \theta] \Delta E + (-k_1 c_B + k_2) \Delta\theta + k_1 (1 - \theta) \Delta c_B \quad (91)$$

Since species B^- diffuses towards the surface, one has

$$\frac{\Delta c_B}{\Delta I_F} = \frac{N(\omega)}{FA} \quad (92)$$

$N(\omega)$ is defined by Eq. (76) or by Eq. (83) according to the hypothesis made on the thickness of the diffusion layer

$$(j\omega\beta + k_1 c_B + k_2) \Delta\theta = [b_1 k_1 (1 - \theta) c_B - b_2 k_2 \theta] \Delta E + k_1 (1 - \theta) N(\omega) \Delta I_F / FA \quad (93)$$

$$[1 - k_1 (1 - \theta) N(\omega)] \Delta I_F = \Delta E / R_{ct} + FA(-k_1 c_B + k_2) \Delta\theta \quad (94)$$

In this case the charge-transfer resistance is:

$$R_{ct} = \left[\frac{\partial E}{\partial I_F} \right]_{\theta, c_B} = \frac{1}{FA[b_1 k_1 (1 - \theta) c_B + b_2 k_2 \theta]} \quad (95)$$

After eliminating $\Delta\theta$ in Eqs. (93) and (94), and replacing θ by its steady state value, when $d\Delta\theta/dt = 0$, i.e.,

$$\theta = k_1 c_B / (k_1 c_B + k_2) \quad (96)$$

the final expression for the impedance can be obtained:

$$Z(\omega) = \frac{1}{FA} \cdot \frac{k_1 c_B + k_2 - k_1 k_2 N(\omega) \left[1 + \frac{-k_1 c_B + k_2}{j\omega\beta + k_1 c_B + k_2} \right]}{k_1 k_2 c_B \left[b_1 + b_2 + \frac{(b_1 - b_2)(-k_1 c_B + k_2)}{j\omega\beta + k_1 c_B + k_2} \right]} \quad (97)$$

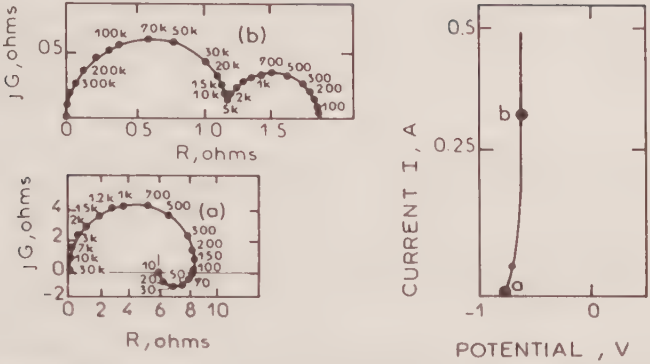


Figure 5. Simulated impedances in the case of heterogeneous reactions [Eq. (98)]. The kinetic parameters are $k_1 = 4 \times 10^8 \exp(36) \text{ V}$; $k_2 = 10^{-3} \exp(10) \text{ V}$; $\beta = 2 \times 10^{-9}$; $c_A = 10^{-4}$; and $C_d = 20 \mu\text{F}$. Impedances (a) and (b) are calculated at polarizations corresponding to points A and B on the simulated polarization curve [from Reference (32)].

In the particular case of a reaction-controlled process the diffusion can be supposed as infinitely fast [$D_i \rightarrow \infty$, hence $N(\omega) = 0$] and therefore the new expression of the impedance is:

$$Z(\omega) = \frac{1}{FA} \cdot \frac{k_1 c_B + k_2}{k_1 k_2 c_B \left[b_1 + b_2 + \frac{(b_1 - b_2)(-k_1 c_B + k_2)}{j\omega\beta + k_1 c_B + k_2} \right]} \quad (98)$$

This expression was calculated for the first time by Gerisher and Mehl for the case of hydrogen evolution.⁽³¹⁾ It can be shown that, according to the values of the parameters in Eq. (98), this impedance can include either a capacitance or an inductance as depicted in Figure 5. In the following chapter (chapter 4), more complicated examples to which these calculations apply will be described.

2.3.3. Numerical Methods for Solving the State Equations (Digital Simulation)

The methods involving large signals often lead to equations that cannot be solved analytically, and therefore one has to use numerical methods treated by a computer. We shall not give here a detailed description of these digital treatments. The reader may refer to basic works published in the literature [for example, References (33), (34), and (35)]. We shall only examine some numerical methods for calculating definite integrals, and for solving ordinary differential and partial differential equations.

The principle of these methods consists in replacing an expression involving infinitesimal increments by a series of discrete operations involving finite differences. The way of transforming the expressions and the size of the differences determine the accuracy of the result and also the time required by the calculation.

2.3.3.1. Numerical Estimation of Definite Integrals

Estimating a definite integral numerically, i.e.,

$$F = \int_a^b f(x) dx \quad (99)$$

where $f(x)$ is a continuous function over $[a, b]$, constitutes a problem in two cases:

- (i) the analytical integral of $f(x)$ is unknown.
- (ii) $f(x)$ is given by a numerical table as a result of an experiment.

The principle consists in approaching F considering a discrete summation on N subintervals:

$$F^* = \sum_{i=0}^N h_i f(x_i) \quad (100)$$

with $x_0 = a$, $x_N = b$, and h_i being coefficients which depend on the method employed.

We shall consider here the case encountered most frequently, i.e., the one where a set of points x_i divides the $[a, b]$ interval into N equal intervals. The error $R(f) = F - F^*$ depends on the number N of points and on the choice of the h_i 's as exemplified below:

- (a) the trapezoid rule. This method involves approximating $f(x)$ with a straight line between x_i and x_{i+1} . In that case:

$$F^* = \frac{b-a}{N} \left[\frac{1}{2}f(a) + \cdots + f(x_i) + \cdots + \frac{1}{2}f(b) \right] \quad (101)$$

and

$$R(f) = -\frac{(b-a)^3}{12N^2} f''(\eta) \quad \text{with } a \leq \eta \leq b \quad (102)$$

Calculation is exact, i.e., $R(f) = 0$, if $f(x)$ is a polynomial of degree one at most.

- (b) the Simpson rule. This rule amounts to approximating $f(x)$ with a parabolic arc for a triplet (x_i, x_{i+1}, x_{i+2}) . In that case:

$$\begin{aligned} F^* = \frac{b-a}{3N} \{ & f(a) + f(b) + 4[f(x_1) + f(x_3) + \cdots + f(x_{2N-1})] \\ & + 2[f(x_2) + f(x_4) + \cdots + f(x_{2N-2})] \} \end{aligned} \quad (103)$$

and

$$R(f) = -\frac{(b-a)^5}{180N^4} f^{(4)}(\eta) \quad \text{with } a \leq \eta \leq b \quad (104)$$

Consequently, the Simpson rule is exact for polynomials of degree three at most. It is used particularly when an accuracy to better than two significant digits is desired.

2.3.3.2. Numerical Integration of Ordinary Differential Equations

Such equations are encountered, for example, when studying the response of heterogeneous electrochemical kinetics to large-amplitude signals. They often require the use of numerical methods when non-linear and when their coefficients are not constant. The form of a first-order equation is:

$$\frac{dy(x)}{dx} = f[x, y(x)] \quad (105)$$

where $y(x)$ is the function to be determined, considering that $y(x_0) = y_0$ (initial value problem).

Let us assume that function y is known at x_i , i.e., $y(x_i)$. The following property is then used:

$$y(x_i + h) = y(x_i) + \int_{x_i}^{x_i+h} (dy/du) du \quad (106)$$

or

$$y(x_i + h) = y(x_i) + \int_{x_i}^{x_i+h} f[u, y(u)] du \quad (107)$$

Two types of step-by-step numerical methods are applied according to whether we consider, for estimating $y(x_i + h)$, the value of $y(x_i)$ only or the values of $y(x_i)$, $y(x_{i-1})$, and $y(x_{i-2})$ together.

2.3.3.2.1. Runge-Kutta methods. Their principles are based on the idea that calculation of $y(x_i + h)$ from $y(x_i)$ can, in principle, be performed using a Taylor expansion of $y(x)$ about $y(x_i)$:

$$y(x_i + h) = y(x_i) + h \frac{dy}{dx}(x_i) + \frac{h^2}{2} \frac{d^2y}{dx^2}(x_i) + \dots \quad (108)$$

Actually, calculation of the successive derivatives of $y = f(x, y)$ with respect to x leads to expressions too complicated to be operative. If we limit ourselves to the first-order derivatives (Euler's method), then the accuracy is insufficient. In order to avoid a calculation of the derivatives of y , it is advisable to express $y(x_i + h)$ with the help of $y(x_i)$ and of certain values of f taken within the $[(x_i, y_i), (x_{i+1}, y_{i+1})]$ interval, i.e.,

$$y(x_{i+1}) = y_i + \alpha_0 K_0 + \dots + \alpha_p K_p \quad (109)$$

where

$$\begin{aligned} K_0 &= hf(x_n, y_n), \\ K_1 &= hf(x_n + \mu_1 h, y_n + \beta_{1,0} K_0), \\ K_2 &= hf(x_n + \mu_2 h, y_n + \beta_{2,0} K_0 + \beta_{2,1} K_1), \text{ etc.} \end{aligned} \quad (110)$$

In identifying Eq. (109) with the Taylor expansion up to the (h^{p+1}) th term one obtains the coefficients μ_i and $\beta_{m,j}$.

The formulae used most frequently derive from a four-term expansion, i.e.,

$$y(x_{i+1}) = y_i + \frac{1}{6}(K_0 + 2K_1 + 2K_2 + K_3) \quad (111)$$

$$K_0 = hf(x_i, y_i)$$

$$K_1 = hf\left(x_i + \frac{h}{2}, y_i + \frac{K_0}{2}\right) \quad (112)$$

$$K_2 = hf\left(x_i + \frac{h}{2}, y_i + \frac{K_1}{2}\right)$$

$$K_3 = hf(x_i + h, y_i + K_2)$$

The error is proportional to 5.

2.3.3.2.2. Predictor-corrector Methods. Calculation of $y(x_{n+1})$ is here considered as:

$$y(x_{i+1}) = y(x_{i-m}) + \int_{x_{i-m}}^{x_{i+1}} f[u, y(u)] du \quad (113)$$

It is to be noted that these methods require the knowledge of $y(x_{i-m}) \dots y(x_i)$. Therefore, it is necessary to use another method to start the calculation (the Runge-Kutta method, for example). We give here the principle of the predictor-corrector methods used in the literature.

An approximate value of a function $y(x_{i+1})$ is determined by extrapolating from the preceding x_i (prediction), i.e.,

$$y^0(x_{i+1}) = y(x_{i-m}) + \sum_{j=i-m}^i B_j f(x_j, y_j) \quad (114)$$

When this first approximate value is determined, a second one can be obtained (correction) using Eq. (115):

$$y^1(x_{i+1}) = y(x_{i-m}) + \sum_{j=i-m}^i A_j f(x_j, y_j) + A_{i+1} f(x_{i+1}, y_{i+1}^0) \quad (115)$$

The procedure is iterated so that

$$y^k(x_{i+1}) - y^{k-1}(x_{i+1}) < \varepsilon \quad (116)$$

2.3.3.3. Numerical Integration of Partial Differential Equations

Partial differential equations appear more particularly in the expression of mass balance when one or several space coordinates are involved. Calculation of the steady state distributions of potential or concentration leads to elliptic equations: for example to the Laplace–Poisson equation, i.e.,

$$\nabla^2 U + f(x, y) = 0 \quad (117)$$

Studying the evolution of these distributions with time leads to parabolic equations, for example to Fick's equation, i.e.,

$$\nabla^2 U - k \frac{\partial U}{\partial t} = 0 \quad (118)$$

Equations (117) and (118) are associated with boundary and initial conditions.

Numerical integration of partial differential equations is performed using finite difference methods. These methods consist in calculating the values of the unknown function at certain points of the plane or the space which form the mesh points of a grid chosen in conformity with the shape of the domain considered (in order to take symmetry into account for example). The derivatives of U are replaced by ratios of finite differences of the function between two neighboring points. Calculation of the values of the function at any mesh point then simplifies into the resolution of a linear system whose dimension is equal to the number of mesh points considered. We shall give two examples of finite difference equations.

2.3.3.3.1. Elliptic Equations. In the case of an elliptic equation, such as:

$$\frac{\partial^2 U}{\partial x^2} + \frac{\partial^2 U}{\partial y^2} = 0 \quad (119)$$

the grid (depicted in Figure 6b), and a mesh point $P_{i,j}$ and its neighboring points P_1, P_2, P_3, P_4 are considered. Let Δx be the step size following the x -axis and the y -axis.

Taylor's expansion of $U(x + \Delta x, y)$, $U(x - \Delta x, y)$, $U(x, y + \Delta y)$, and $U(x, y - \Delta y)$ allows one to replace, to the second order, the equation (119) to be solved at point $P_{i,j}$ by the algebraic equation depending on the values of U at points $P_{i,j}, P_1, P_2, P_3$, and P_4 :

$$\frac{1}{\Delta x^2} (U_{i+1,j} - 2U_{i,j} + U_{i-1,j}) + \frac{1}{\Delta y^2} (U_{i,j+1} - 2U_{i,j} + U_{i,j-1}) = 0 \quad (120)$$

By writing a similar relation for all the mesh points of the domain considered within the (x, y) plane and by expressing in a similar way the boundary conditions, one obtains a linear system. Hence in terms of a matrix form: $A\mathbf{u} = B$. The properties of matrix A enable, in general, the system to be readily solved using classical iteration methods^(33,34) starting from arbitrary values of U and describing the grid row-by-row or column-by-column.

2.3.3.3.2. *Parabolic Equations.* In the case of a parabolic equation, such as

$$\frac{\partial^2 U}{\partial x^2} = \frac{\partial U}{\partial t} \quad (121)$$

finite difference equations can, in principle, be established in a similar way to that used for elliptic equations. However, integrating these equations gives rise to difficult problems of stability depending on the size of the time increment Δt chosen.

A finite difference equation which is exact to the second order both with respect to x and t , and assures stability, is known as the Crank–Nicholson equation. This equation relies on a particular estimation of $(\partial^2 U / \partial x^2)$ as a function of the values of U at mesh points (Figure 6a):

$$\left(\frac{\partial^2 U}{\partial x^2} \right)_{i,(n+1)/2} \approx \frac{1}{2} \left(\frac{U_{i+1,n} - 2U_{i,n} + U_{i-1,n}}{(\Delta x)^2} + \frac{U_{i+1,n+1} - 2U_{i,n+1} + U_{i-1,n+1}}{(\Delta x)^2} \right) \quad (122)$$

Therefore Eq. (121) can be written as:

$$\begin{aligned} U_{i-1,n+1} + \left[-2 - \frac{2(\Delta x)^2}{\Delta t} \right] U_{i,n+1} + U_{i+1,n+1} \\ = -U_{i-1,n} + \left[2 - \frac{2(\Delta x)^2}{\Delta t} \right] U_{i,n} - U_{i+1,n} \end{aligned} \quad (123)$$

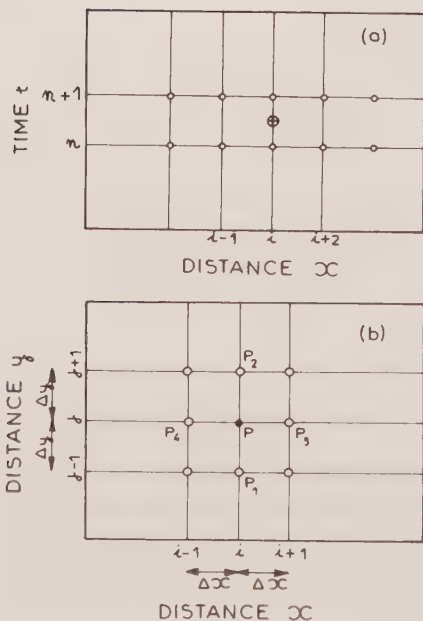


Figure 6. Grid points for the discretization of (a) parabolic problems and (b) elliptic problems.

Numerical algorithms for solving this equation are given in Reference (35).

It can be noted that these methods allow one to solve certain types of non-linear equations such as the equation describing the simultaneous contributions of diffusion and of non-first-order homogeneous chemical reactions.

2.3.4. Analog Simulation

Instead of calculating the response of a model, it is possible to simulate this response using an analog device, which is sometimes called a dummy cell. In addition to the equivalent circuits realized with discrete components (resistors, self-inductors, capacitors) some authors have used distributed parameter devices leading to transfer functions varying with frequency like $\omega^{1/2}$, in order to simulate diffusion-controlled processes.⁽³⁶⁾

3. General Considerations on Measurement Methods

The principles described in this section deal with electric quantities, but they apply to all other control quantities (T, P, c_i^*, A, Ω). Before using any non-steady state technique one has to stabilize the steady state polarization point of interest. Therefore the principles of polarization control will be first examined.

3.1. Polarization Control

3.1.1. Principles of Polarization Control⁽³⁷⁾

The first galvanostatic supplies imposing a direct current allowed one to undertake the study of out-of-equilibrium electrochemical systems. But soon a difficulty arose in the case of metal-electrolyte interfaces whose current-potential curve has a part with a negative slope (Figure 1a), this part being inaccessible with this type of regulation. An important improvement was realized when potentiostats began to be used because they allowed one to control the whole of the characteristic curve. With such devices many experimental problems encountered in electrochemistry have been solved satisfactorily. However, it has been observed that oscillation and commutation phenomena sometimes persist even when a potentiostat is used, and it has been shown that certain electrochemical systems remain inaccessible even with a potentiostatic regulation. To solve this problem, it is necessary to consider the principle of the regulation in a different way, in particular by taking account of the role of the load-line.

3.1.2. Misfit of the Polarization Device

In general, oscillations and commutations seem to be related to phenomena that appear when a system is shifted from its equilibrium state. These phenomena are directly related to the interactions between the system and its environment which arise from the constraint imposed on the system studied. The constraint is usually described as an independent variable (for example, the potential in electrochemistry), because it is considered that the system does not react with its environment, constituted by the reservoir, the thermostat, the ambient medium, the regulation device . . . as the case may be. In this case, the control quantity, chosen by the experimenter, is transmitted to the system without any modification, and the system-environment interactions can be neglected. The steady state characteristic is plotted by varying the constraint imposed and by measuring the change of a quantity characterizing the state of the system. When electric quantities are used, the characteristic curve represents the overall current I passing through the interface considered, to which a potential E_{ref} , i.e., the potential difference between the reference electrode and the working electrode, is applied.

Figure 7 depicts some examples of non-linear current-potential curves. Types (a) and (b) are relative to potential-controlled systems; types (a) and (c) to current-controlled systems whereas systems of type (d) can be controlled by neither control quantity. This means that the state of systems characterized by (a) or (b) can be determined unambiguously by applying a given potential difference to the interface. This is also the case if a given current is applied to systems characterized by (a) and (c). In contrast, if a current is applied to (b) or a potential to (c) or either a current or a potential to (d), there can be three possible states and the system is called a multi-steady state system. It is thus clear that a system presents multi-steady states both when it exhibits a certain extent of complexity and when the constraint, which displaces it from its equilibrium state, is not matched with the case considered.

However, the experimental steady state characteristics of multi-steady state systems, are not, in general, similar to those depicted in Figure 7 (solid lines), because the constraint is generally imposed as an independent variable and, if it is not well-matched, potential jump phenomena are observed leading to hysteresis loops. Thus, when the value of the constraint [current for (b), potential for (c) and (d)] increases, a steep jump appears in the value of the observable quantity (point A). When the constraint is decreased a similar phenomenon is observed in the opposite direction (point B). Experimentally a hysteresis loop O-A-A'-M-B-B'-O is obtained which is often characteristic of a multi-steady state system. It is noteworthy that the states characterized by the branch AB are inaccessible in this case.

3.1.3. How to Match the Regulation with the System

When the experimental characteristic curve of a steady state system exhibits both steep jumps and a hysteresis loop, it is necessary to find out

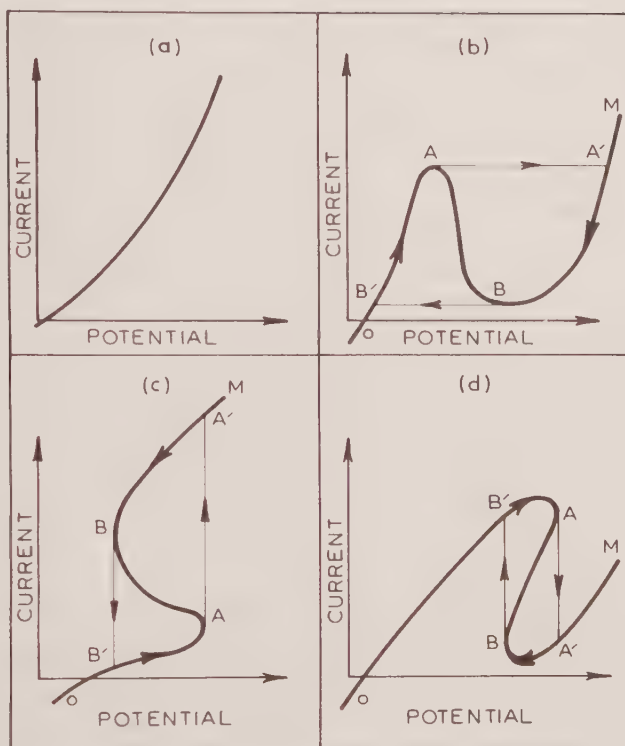


Figure 7. Examples of non-linear current-potential curves [from Reference (37)]: (a) exponential-shaped curve: potential or current-controlled interface; (b) N-shaped curve: potential-controlled interface; (c) S-shaped curve: current-controlled interface; (d) Z-shaped curve. O-A-A'-M-B-B'-O hysteresis observed on the current-potential curve for multi-steady state interfaces.

whether or not there exist intermediate states like those on branch AB (Figure 7) by trying to match the constraint with the system. As a matter of fact, if such intermediate states exist, the interpretation of the phenomenon can be entirely different. In this case, it is of primary interest to investigate the intermediate states for it is generally very difficult to determine the properties of a process just by referring to the two extreme states (points B' and A' in Figure 7) without any information on the transition between them.

Generally the initial state is assumed to be the state of the system in the absence of any constraint ($I = 0$). This state at rest (which is sometimes the thermodynamic equilibrium state) will be supposed unique and stable. The problem is now how to reach experimentally the state to be studied and how to control it. This is performed by using an external constraint described by a set of equations called the control law. This law is subjected to the input quantities which are themselves chosen by the experimenter. In the case where the system and its environment presents several possible equilibrium states, it is necessary to establish, by using this control law, which are the states that

can be reached starting from the state at rest (point O in Figure 7). In fact only the accessible *and* stable states can be studied experimentally.

Let us consider the system presenting the current–potential characteristic shown in Figure 7d (a Z-shaped characteristic). This is indeed the most critical case since the state of such a system is not determined unambiguously either by the current I which passes through it, or by the potential difference E_{ref} which is applied to it. Note, that all problems due to stability, which cannot be neglected in practice, will be disregarded in this simplified study.

Since in the case of systems exhibiting a Z-shaped characteristic the states are defined by both I and E_{ref} , one will have to act on these two quantities in order to control a particular state. The control law will hence be a function of both I and E_{ref} . In general, a regulation which imposes a time-independent control law has to be realized. In that case the control law is reduced to a relationship between I and E_{ref} which depends neither on the derivatives nor on the integrals of these quantities with respect to time and which will be taken as linear for the sake of simplicity:

$$E_0 = E_{\text{ref}} + \mathcal{R}I \quad (124)$$

where E_0 is the input quantity and $\mathcal{R}$ a chosen parameter. This type of constraint is usually called a load-line (Figure 8a).

In order to determine the values of the parameters E_0 and $\mathcal{R}$ which define the position of the load-line, we plot (Figure 8b), in a (E_{ref}, I) plane, the characteristic $f(I, E_{\text{ref}}) = 0$ and the straight line represented by Eq. (124). We shall consider that a polarization point $M(E_{\text{ref}}, I)$ is a working point if at least one couple $(E_0, \mathcal{R})$ can be found such that the load-line intersects $f(I, E_{\text{ref}}) = 0$ at point M without being tangent to this curve. It can be shown⁽³⁷⁾ that if the load-line is tangent to the curve at point M, the system is destabilized. In

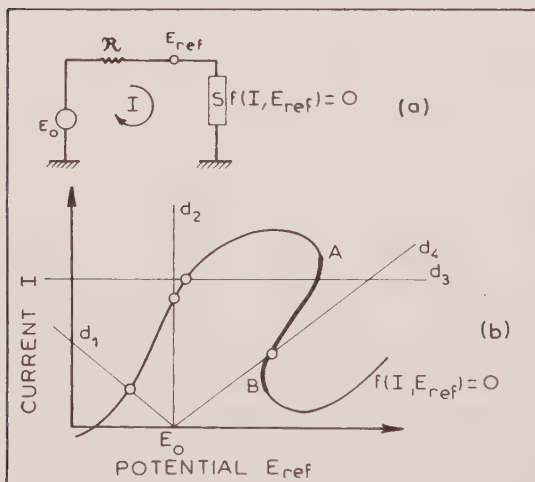


Figure 8. Regulation of the polarization of a multi-steady state system S, characterized by a current–potential relationship $f(I, E_{\text{ref}}) = 0$ [from Reference (137)]. (a) Equivalent circuit of a regulation controlling the polarization of the system S (E_0 is the voltage supply and $\mathcal{R}$ the internal resistance). (b) Polarization curve of the multi-steady state system S with the four typical positions of the load-line: d_1 defined by $\mathcal{R} > 0$ (potentiometric regulation); d_2 defined by $\mathcal{R} = 0$ (potentiostatic regulation); d_3 defined by $\mathcal{R}$ infinite (galvanostatic regulation); d_4 defined by $\mathcal{R} < 0$ (negative impedance regulation).

order that the state corresponding to M be accessible, it is furthermore necessary that a continuous succession of equilibrium states be found between the state at rest and the polarization point considered. Thus, it will be possible to find a continuous transition between these two states by varying either E_0 or $\mathcal{R}$ or both of them. The four typical positions of the load-line are depicted in Figure 8b.

Note that the preceding reasoning explains the existence of the hysteresis loop often observed experimentally with multi-steady state systems. In fact, if such a system is polarized using a potentiostat (d_2 parallel to the current axis), at points A or B the load-line becomes tangent to the curve $f(I, E_{\text{ref}}) = 0$ at the polarization point imposed, and a destabilization occurs (see Figure 7d). The interface-regulation system jumps to a new polarization point (A' or B') respectively, which is the stable equilibrium point of the configuration.

It can be seen that, by realizing a supply imposing a load-line such as d_4 , it is possible to explore the branch AB (Figure 7). An electronic supply having this property can be realized using a negative impedance converter⁽¹²⁾ which will allow a complete investigation of systems exhibiting such a characteristic.

3.2. Non-steady State Techniques

3.2.1. Classification of Non-steady State Techniques

We have seen above that there exist two types of constraints imposed at the electrochemical interface, those that can be and those that cannot be controlled by the experimenter. This leads to two different types of techniques, i.e., the relaxation techniques and those based on the analysis of the spontaneous fluctuations.

The principle on which the relaxation techniques are based is that the steady state depends on a certain number of quantities (E_{ref} , T , P , A , c_i^* , Ω). If these quantities are modified by the experimenter, the state of the system will be altered. The rate at which the system tends towards a new steady state depends on certain characteristic parameters such as, for example, the reaction rate constants, the diffusion coefficients, etc. Analysis of the transition towards this new state will hence provide information on these parameters and the phenomenological equations that relate them mutually. Although the techniques used most frequently are based on electric perturbations we shall see below that techniques based on the other five quantities (T , P , A , c_i^* , Ω) can also be used.

Analysis of the spontaneous fluctuations of the quantities observed about a polarization point (generally the current or the potential in electrochemistry) can be classified in two categories according to their amplitude. The low-amplitude fluctuations are called electrochemical noise which is related to stochastic processes at the interface. The high-amplitude fluctuations are generally considered as oscillations of the electrochemical system and studying

them requires the use of techniques based on the analysis of the oscillations in non-linear systems.

3.2.2. *How to Choose a Non-steady State Technique Satisfying the Aim of the Electrochemist*

If only the values of certain parameters of an already known mechanism are to be estimated, it is possible to use a special measurement signal, or a special data treatment, which sensitizes the parameter investigated. This will be illustrated in the case of the double potential step method applied to consecutive redox processes, and in the case of the method based on plotting the experimental results versus $t^{1/2}$ in order to approach the diffusion parameters.

However, if a model for an unknown interface is to be elaborated, it is necessary to use a wide spectrum measurement signal which excites all the natural frequencies of the system. The best example is given by the measurement of the impedance over a wide frequency range.

3.2.3. *General Considerations on the Experimental Devices Used in Non-steady State Techniques*

Using such techniques requires, in addition to the interface polarization regulation, a means of data acquisition and a data treatment that fulfill certain criteria. These criteria are defined from the classical properties of signal processing, i.e., bandwidth, signal-to-noise ratio, linearity, drift, and detection.

(a) *Bandwidth*. Since the signals imposed and analyzed are time-dependent, it is necessary to define a minimum bandwidth (or a maximum rise-time) in order not to distort the measurement signals.

(b) *Signal-to-noise ratio*. The experimental set-up to be used must be low-noise in order that an adequate signal-to-noise ratio be obtained without altering too much the accuracy of the measurement. This ratio defines the lowest amplitude of the measurement signal and limits the small-signal analysis of non-linear systems.

(c) *Linearity*. In the case of small-signal analysis, the amplitude must range between two frequency-dependent limits, which define the range within which linearity is satisfied. The higher limit is defined by the maximum amplitude that can be accepted if the system is to be considered as linear. Linearity is checked by increasing the amplitude from a very low value. When the quantity measured (generally the impedance) varies, linearity is no longer followed. As was said before, the lower limit is defined in terms of the signal-to-noise ratio.

(d) *Drift*. The set-up used must have a very high stability with respect to time. Thus drift must be very small, for the processes to be studied are often rather slow.

(e) *Detection*. The problem of data acquisition and signal processing becomes more critical when very accurate measurements have to be performed, in particular in the case of small-signal analysis.⁽³⁸⁾ Information theory shows that the optimum detection of a signal is performed using a correlation method which gives the maximum accuracy with a given signal-to-noise ratio. These techniques have been used hitherto to measure (i) impulse responses by applying a white noise and using a correlator,⁽³⁹⁾ and (ii) impedance by applying a sinusoidal signal and using a transfer function analyser⁽⁴⁰⁾ or synchronous detectors⁽⁴¹⁾. Because of their detection principles, step-response techniques are not as accurate as those used to measure impulse responses and impedances, except when using an averaging technique which eliminates spurious noises.

In addition, in many cases, measurements must often be performed at very low frequencies (down to 10^{-3} Hz) or over very long times, which is equivalent. This necessitates the use of digital technology for the detector, since analog technologies can be used only at frequencies higher than about 1 Hz.

4. Electrical Relaxation Techniques

Although the applicability of the electrical relaxation methods was foreseen long ago,⁽⁴²⁾ it is only thanks to improvements in electronic instrumentation that they have been developed. Therefore, before classifying all the electric techniques relative to the possible shapes of the analysis signal and to the nature of the input quantity, we shall present some general considerations on electric instrumentation (see also chapter 10).

In addition to the electrolytic cell (generally a three-electrode one), we shall also consider four important parts which must be present in the experimental set-up (Figure 9):

(i) Since the electrochemical interface has to be polarized it is necessary to use a polarization device: potentiostat, galvanostat, or negative output resistance regulation.

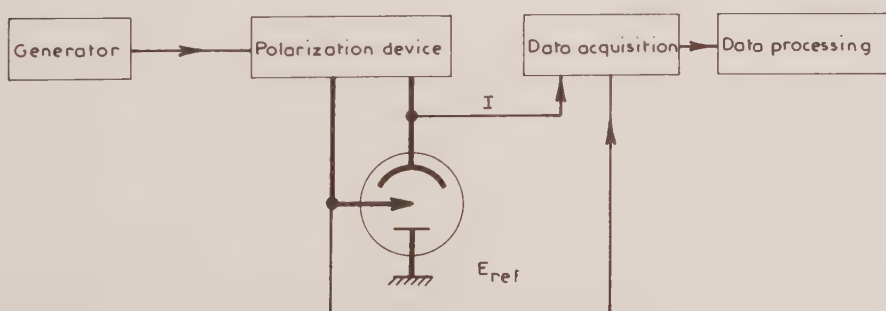


Figure 9. Synopsis of the measurement set-up.

(ii) Since the control is time-dependent, it is necessary to use a generator which will supply the analysis signal (sinusoidal, impulse, ramp, pseudo-random white noise . . .).

(iii) The response of the system will be analyzed by a data acquisition system. In general, it is necessary to employ amplifiers to measure the potential and the current. They can be differential or not, but they must always have a high input impedance (if the current is measured across a resistor inserted in the secondary electrode channel) in order that the electrochemical system be isolated from the data acquisition device. They must often provide a continuous potential offset in order to match the response signal with the recording or analysis apparatus.

(iv) If the data treatment is not performed in-line, a previous recording must be made. For example a transient recorder is often helpful when the signal is not repetitive (impulse or ramp signal).⁽⁴³⁾ At this stage, the device used will markedly depend on the shape of the signal and on the possibility of using a computer or not.

Two severe limitations of the electrical techniques come from the electrolyte resistance and double-layer charging (Figure 3). The finite conductivity of the electrolyte limits the use of the non-steady state techniques by adding a parasitic ohmic drop in series with the faradaic voltage. When this ohmic drop is large compared with the latter it will be difficult to obtain accurate results on faradaic processes. Potentiostatic techniques are basically affected. Electronic compensations or/and Haber-Luggin capillary technique could be used to cancel out ohmic drop. Double-layer charging limits the usefulness of almost all non-steady state measurements in the sub-microsecond range by "short circuiting" the higher frequency (shorter time) processes. The galvanostatic double pulse technique tries to cancel out the influence of the charging current by separating it from the faradaic processes.

We shall now describe the techniques which are mainly based on the use of a ramp, a step, and an exponential signal. The use of a sinusoidal signal will be described in chapter 4.

4.1. Ramp Techniques

The well-known potential sweep voltammetry⁽⁴⁴⁾ consists in applying a single or cyclic potential ramp [Table 1(a)], using a potentiostat, and in analyzing the corresponding current response. Although this method is easy to employ experimentally, theoretical calculations on models are rather complicated and generally require the use of a computer.

This method allows one to check the reversibility of a redox couple, to establish whether several steps are involved in a reaction mechanism, to study the adsorption-desorption process, and to detect electroactive intermediates. Since the sweep rate can be varied over a wide range, this method allows the investigation of slow as well as fast reactions.

Theoretical calculations of models markedly depend on the case considered, since the method involves large signals and since the potential sweep range is generally very broad. Two types of treatment are expected.

(i) If charge transfer takes place in a single step at the electrode and is only controlled by the diffusion of the reactants, then the semi-analytical treatment leads to an integral equation such as Eq. (67) (whether or not the mechanism analyzed implies homogeneous chemical reactions).

(ii) If charge transfer is considered to occur in several steps involving adsorbed intermediates, it will be necessary to use a numerical method for integrating the differential equations accounting for the behavior of the system.

4.1.1. Charge Transfer Occurring in a Single Step⁽⁴⁵⁾

Particular attention has been devoted to the case of diffusion-controlled charge transfer (reversible or nonreversible). This possibility is often the limiting case which one will try to reach by changing the experimental conditions (sweep rate, initial concentrations ...).

4.1.1.1. Single Sweep Technique

As was seen above, the processes taking place at an interface at which a diffusion-controlled redox process takes place are governed by the integral equation (67) provided that the Nernst equation applies (and that $c_{Red}^* = 0$). When a potential

$$E(t) = E_i - vt \quad (125)$$

is applied, E_i being the initial potential chosen so that species Ox is not reduced, and v being the potential sweep rate, then the following integral equation is obtained:

$$\int_0^t \frac{I_F(\theta) d\theta}{(t-\theta)^{1/2}} = \frac{nFAc_O^*(D_O\pi)^{1/2}}{1 + \left\{ \exp \left[\frac{nF}{RT} (E_i - E^\circ) \right] \exp \left[\frac{nF}{RT} (-vt) \right] \right\} (D_O/D_R)^{1/2}} \quad (126)$$

or

$$\int_0^t \frac{I_F(\theta) d\theta}{(t-\theta)^{1/2}} = \frac{nFAc_O^*(D_O\pi)^{1/2}}{1 + \exp \left\{ \frac{nF}{RT} [E(t) - E_{1/2}] \right\}} \quad (127)$$

where $E_{1/2}$ is the half-wave potential, i.e.,

$$E_{1/2} = E^\circ + \frac{RT}{nF} \ln (D_R/D_O)^{1/2} \quad (128)$$

Three different methods have been proposed to solve Eq. (126).

- (i) *Numerical solution:* The time between $t = 0$ and $t = T$ is divided into N intervals, and the left member is integrated by parts. N algebraic equations of an unknown function $I_F(\chi)$ are obtained therefrom, χ being equal to N/T , such as:

$$2\left(\frac{Ta}{N}\right)^{1/2} \left\{ I_F(1)\chi^{1/2} + \sum_{i=1}^{\chi-1} (\chi^{-i})^{1/2} [I_F(i+1) - I_F(i)] \right\} = G(\chi) \quad (129)$$

where G , a function of time, is the right-hand member of the integral equation (126) and $a = nF/RT$.

- (ii) *Semi-analytical solution:* The integral equation (126) is an Abel equation whose solution is:

$$I_F(at) = \frac{G(0)}{\pi(at)^{1/2}} + \frac{1}{\pi} \int_0^{at} \frac{1}{(at-z)^{1/2}} \left[\frac{dG(z)}{dz} \right] dz \quad (130)$$

- (iii) *Series expansion solution:*⁽⁴⁶⁾ The solution is in this case

$$I_F(t) = \frac{1}{\pi} \sum_{j=1}^{\infty} (-1)^{j+1} j^{1/2} \exp \left[-j \frac{nF}{RT} (E - E_{1/2}) \right] \quad (131)$$

Thus, whatever the method used, a computer must be employed in order to compare the experimental results with the model considered. Comparison is generally performed by considering the characteristic parameters of the voltammograms, mainly the current I_{Fp} and the potential E_p of the peak (see Figure 10).

For a diffusion-controlled reversible transfer, the following values have been calculated:

$$I_{Fp} = 0.4463 nFA(D_O nFv/RT)^{1/2} c_O^* \quad (132)$$

$$(E_p - E^\circ)n + \frac{RT}{F} \ln(D_O/D_R)^{1/2} = -28.50 \pm 0.05 \text{ mV} \quad (133)$$

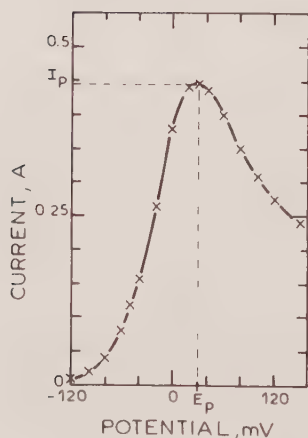


Figure 10. Simulated voltammogram according to the data of Reference (44) (E_p is the peak potential and I_p the peak current).

However, the peak of a voltammogram is rather broad and the half-peak potential is often used:

$$E_{p/2} = E^\circ + \frac{RT}{nF} \ln (D_R/D_O)^{1/2} + 1.09 \frac{RT}{nF} \quad (134)$$

Thus, n , D_O and c_O^* can be determined.

Voltammograms and their characteristic parameters have also been calculated when homogeneous chemical reactions are coupled with charge transfer in the following cases:^(44,47,48)

- (i) a reversible chemical reaction preceding an either reversible (case III) or irreversible (case IV) transfer.
- (ii) A charge transfer followed by an either reversible (case V) or irreversible (case VI) chemical reaction.
- (iii) A catalytic reaction coupled to an either reversible (case VII) or irreversible (case VIII) charge transfer.
- (iv) A charge transfer coupled with a chemical reaction of an order equal to or higher than two (dissociation of dimers, disproportionation, and dimerization).
- (v) An ECE mechanism (Electrochemical–Chemical–Electrochemical).

In each of these cases, the influence of the chemical reaction on the voltammogram will depend on its reaction rate compared with the potential sweep rate. If a fast reaction is involved with a very low sweep rate, the voltammogram will almost entirely be controlled by the chemical reaction and will correspond to the kinetic current. If the sweep rate is high compared with the reaction rate, the curves will be similar to those observed with pure transfer and will correspond to the diffusion current.

The problem is how to characterize, at least qualitatively, an unknown system. To this end, several diagnostic criteria have been established. For example, one can plot (Figure 11):

$$\frac{I_{Fp}}{nFA(D_O v)^{1/2} c_O^* \left(\frac{nF}{RT} \right)^{1/2}} \quad \text{or} \quad \frac{\Delta E_{p/2}}{\Delta \log v} \quad (135)$$

as a function of v . Using diagrams such as those in Figure 11, one can characterize the mechanism studied by analyzing the change of the characteristic parameters of the voltammogram when varying the sweep rate.

In addition, it can be seen that, for extreme values of the parameters corresponding to pure diffusion currents or to kinetic currents, the equations of the voltammograms as well as the variations of the peak current and the peak potential are considerably simplified. Consequently, the state parameters will be easier to approach and the diagnostic criteria simpler to apply, in the zones which are characteristic of the different types of behavior. It is therefore very important to determine the values of the parameters constituting the

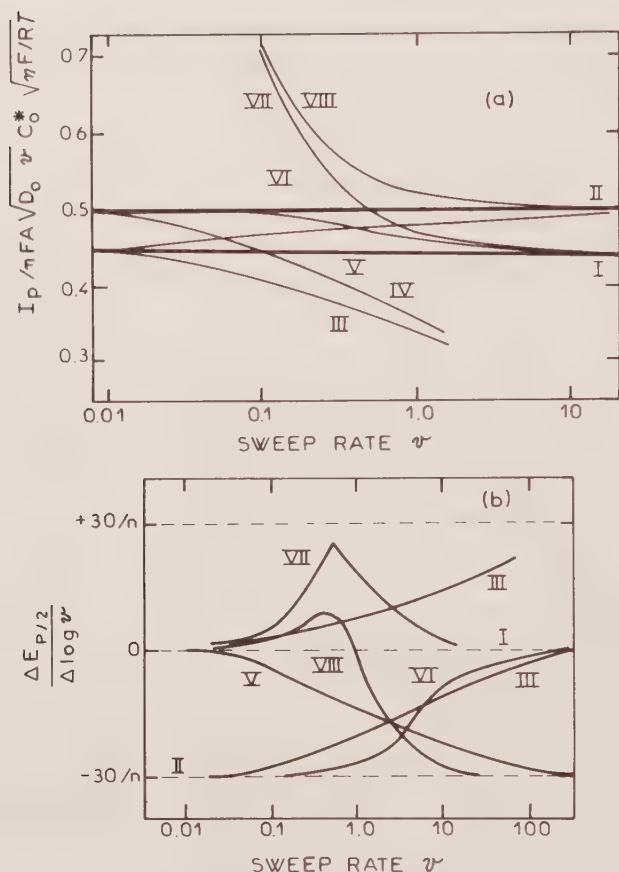


Figure 11. Examples of diagnostic criteria from Reference (44) for different mechanisms. (a) Variation of peak current functions with the potential sweep rate. Case I: irreversible transfer; II: reversible transfer; III, IV, V, VI, VII, VIII described in Section 4.1.1.1. (b) Rate of the potential shift as a function of the sweep rate ν .

limits of these zones (Figure 12). Experimentally, whenever possible, it is also interesting to change the values of the experimental parameters in order to bring the voltammogram into a zone where the behavior can be characterized more readily.

4.1.1.2. Reverse and Cyclic Voltammetry

Instead of analyzing a single peak, a backward sweep [Table 1(b)] can be used immediately after the forward sweep, and a second peak, of the same height, corresponding to the reverse process, can be obtained in the case of a reversible electron transfer. However in the case of a more complex process, more complicated voltammograms are obtained (Figure 13). The sweeping procedure is repeated periodically in cyclic voltammetry.

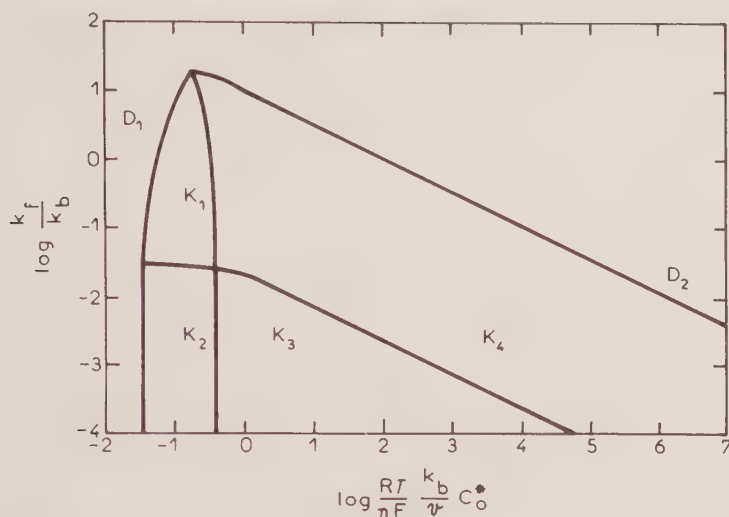


Figure 12. Diagram defining the zones of existence of the different types of currents for a first-order chemical reaction ($A + B \xrightleftharpoons[k_b]{k_f} C + D$) preceding a reversible charge-transfer process [from Reference (47)]. Character of the voltammogram: D_i , diffusion control; K_i , kinetic control (i denotes small differences of character).

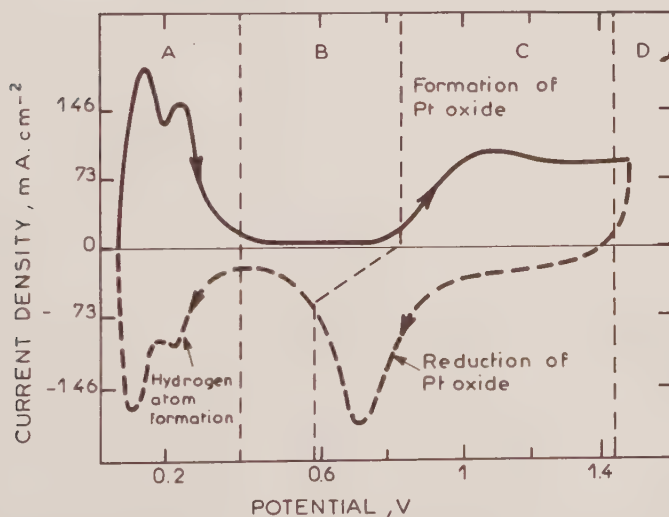


Figure 13. Experimental curve of the reverse sweep voltammetry (forward and backward) for a surface process: the adsorption of hydrogen on a platinum electrode [from Reference (49)].

In opposition to single sweep voltammetry, cyclic voltammetry cannot give the kinetic parameters with accuracy, since the equations generally used apply only when there are no concentration gradients in the solution just before the sweep starts. Although several attempts at a theoretical support of cyclic voltammetry exist, few quantitative data have been obtained with this method (see chapter 4.1.2), which is generally restricted to a rapid but qualitative elucidation of reaction mechanisms.

Cyclic voltammetry has been widely used in analyzing adsorption-desorption processes at solid electrodes, in particular involving oxygen and hydrogen.^(49,50) The number and the position of the anodic and cathodic peaks allow one to ascertain the different types of surface bonding and to estimate the reversibility of the phenomenon (Figure 13). Determining the electric charge related to the various peaks enables one to evaluate the fractional coverage of the surface.⁽⁵¹⁾

4.1.1.3. Convolutional (or Semi-integral) Potential Sweep Voltammetry

Linear potential sweep voltammetry exhibits a certain number of disadvantages:^(52,53)

- (i) The faradaic current cannot be readily separated from the charging current of the double layer capacity.
- (ii) It is difficult to correct the experimental results for the ohmic drop which causes marked distortions of the voltammogram by shifting the peak towards higher potential values, by diminishing the peak current, and by increasing the width of the peak.
- (iii) It is necessary to know the kinetic law *a priori*.
- (iv) Only the information relative to the peak is exploited.

A more rational utilization of the voltammograms has been proposed by Saveant (Convolutional potential sweep voltammetry method)⁽⁵⁴⁻⁵⁶⁾ and by Oldham (Semi-integration method),⁽⁵⁷⁻⁵⁸⁾ simultaneously. These two proposed methods consist in analyzing the convoluted current $\hat{I}_F$, calculated using a computer, instead of the current I_F :

$$\hat{I}_F(t) = \frac{1}{\pi} \int_0^t \frac{I_F(\theta)}{(t-\theta)^{1/2}} d\theta \quad (136)$$

As a matter of fact, it can be derived from the integral equation (127) that in a diffusion-controlled electron transfer:

$$\hat{I}_F = \frac{nFAc_O^*(D_O)^{1/2}}{1 + \exp \left[\frac{nF}{RT} (E - E_{1/2}) \right]} \quad (137)$$

and hence that:

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{\hat{I}_{F1} - \hat{I}_F}{\hat{I}_F} \quad (138)$$

where $\hat{I}_{Fl} = nFAc_O^*(D_O)^{1/2}$ is the limiting value of $\hat{I}_F$ when $E \rightarrow -\infty$. Similarly, the concentrations $c_O(0, t)$ and $c_R(0, t)$ of species *Ox* and *Red* at the interface can be written by virtue of Eqs. (63) and (64) as:

$$\frac{c_O(0, t)}{c_O^*} = 1 - \frac{\hat{I}_F}{\hat{I}_{Fl}} \quad (139)$$

and

$$\frac{c_R(0, t)}{c_O^*} = \frac{\hat{I}_F}{\hat{I}_{Fl}} \left(\frac{D_O}{D_R} \right)^{1/2} \quad (140)$$

Consequently, this method leads to particularly simple diagnostic criteria, since straight lines are obtained when $\ln[(\hat{I}_{Fl} - \hat{I}_F)/\hat{I}_F]$ is plotted versus E (logarithmic analysis). Only the slope and the intercept with the potential axis have to be determined in order to obtain n and $E_{1/2}$ (Figure 14). All information contained in the voltammogram is exploited here. The results are therefore more accurate with this diagnostic procedure than with the classical sweep voltammetry.

This type of logarithmic analysis has been used for a wide variety of reaction mechanisms. The results are summarized in Table 2. It can be seen that the slope is always RT/nF (i.e., 59.1/ n mV at 25°C on the basis of common logarithms).

Separating the faradaic component from the overall current and correcting for the ohmic drop are much simpler with this method whatever the reaction mechanism considered. For example, if the double-layer charging current is small with respect to the faradaic current (i.e., for moderate v values) then the voltammogram is influenced only by the ohmic drop. In this case, it is sufficient to plot the convoluted current $\hat{I}_F$ as a function of $E_{ref} = E + R_e \hat{I}_F$

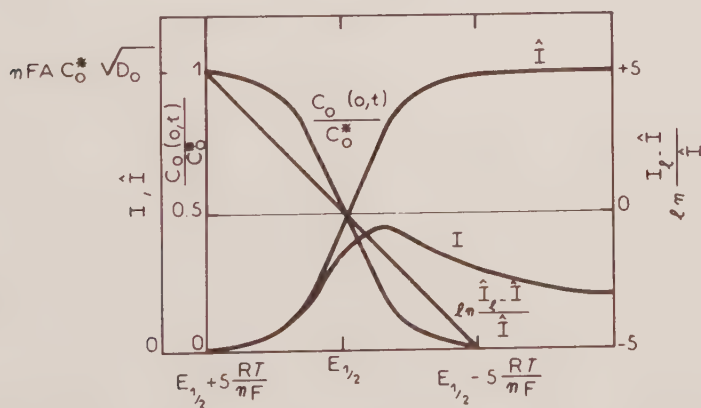


Figure 14. Convolution procedure for analyzing a voltammogram in the case of pure diffusion control: current I , convoluted current $\hat{I}$, surface concentration, and logarithmic analysis [from Reference (55)].

Table 2
Chemical Polarization. Logarithmic Analysis (from [55]).

Reaction scheme	Logarithmic analysis (neperian logarithms)
Pure diffusion control $A + ne \rightleftharpoons B$ (E^0)	$E = E^0 + \frac{RT}{nF} \ln \frac{\hat{I}_F - \hat{I}_F}{\hat{I}_F}$
Antecedent first order reaction $A \xrightleftharpoons[k_b]{k_f} B \quad B + ne \rightleftharpoons C$ (E^0) (K)	$E = E^0 - \frac{RT}{2nF} \ln k_b + \frac{RT}{nF} \ln \frac{\hat{I}_F - \hat{I}_F}{\hat{I}_F}$
Consecutive first order reaction $A + ne \rightleftharpoons B \quad B \xrightarrow{k} \text{products}$ (E^0)	$E = E^0 + \frac{RT}{2nF} \ln k + \frac{RT}{nF} \ln \frac{\hat{I}_F - \hat{I}_F}{\hat{I}_F}$
Consecutive dimerization $A + ne \rightleftharpoons B \quad 2B \xrightarrow{k} \text{products}$ (E^0)	$E = E^0 + \frac{RT}{3nF} \ln \frac{2}{3} \frac{k}{nFSD} + \frac{RT}{nF} \ln \frac{\hat{I}_F - \hat{I}_F}{\hat{I}_F^{2/3}}$
ECE and disproportionation: ECE (1) $A + ne \rightleftharpoons B$ (E^0) (2) $B \xrightleftharpoons[k_b]{k_f} C$ (K)	(3) $C + ne \rightarrow D$ DISP1 (4) $B + C \xrightarrow{k_d} A + D$ DISP2 (4) $B + C \xrightarrow{k_d} A + D$
	$E = E^0 + \frac{RT}{2nF} \ln \frac{k}{(1+K)^2} + \frac{RT}{nF} \ln \frac{\hat{I}_F - \hat{I}_F}{\hat{I}_F}$ $E = E^0 + \frac{RT}{2nF} \ln \frac{k}{2(1+K)} + \frac{RT}{nF} \ln \frac{\hat{I}_F - \hat{I}_F}{\hat{I}_F}$ $E = E^0 + \frac{RT}{3nF} \ln \frac{k_d}{6KnFAD} + \frac{RT}{nF} \ln \frac{\hat{I}_F - \hat{I}_F}{\hat{I}_F^{2/3}}$
for ECE mechanism : reaction (4) is negligible, and the rate determining step is reaction (2)	
for DISP 1 " : " (3) " " " " " " " " " (2)	
for DISP 2 " : " (3) s " " " " " " " " " (4)	
(k = k _f + k _b , K = k _f /k _b : equilibrium constant)	

instead of E . However, it has been shown that more accurate results are obtained when the electrolyte resistance is as small as possible. This implies that a compensation of ohmic drop has to be used.

The main advantage of convolutive voltammetry is that the concentrations of the diffusing species at the electrode surface can be directly derived from the convoluted current $\hat{I}_F$. Thus, the convolution procedure appears as a mathematical tool for eliminating the diffusion polarization from the experimental data.

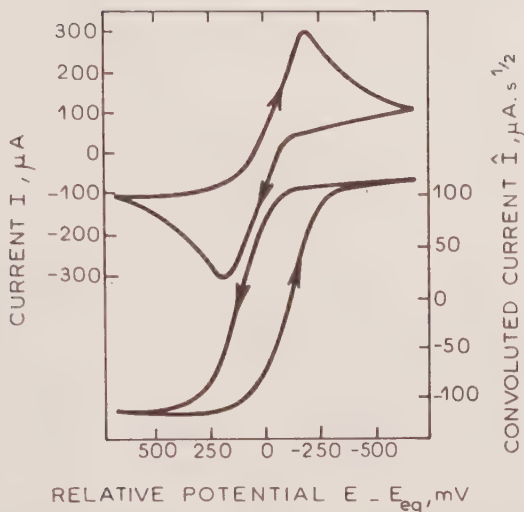


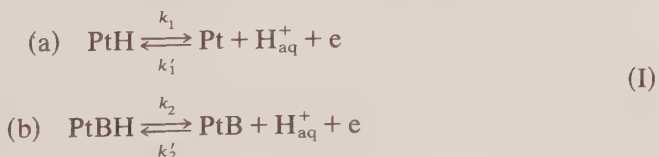
Figure 15. Cyclic voltammogram (upper curve and left-hand scale) and cyclic convoluted current (lower curve and right-hand scale) derived from it in the case of a quasireversible electron transfer [from Reference (61)].

In addition, considering the form of the equations, the curve $\hat{I}_F$ versus E does not depend on the exact shape of the potential sweep in the case of diffusion-controlled systems. Therefore this logarithmic analysis of voltammograms can be applied to cyclic voltammetry (and other techniques, as will be seen below). Thus, when the reaction mechanism only involves charge transfer steps or homogeneous chemical reactions which remain at equilibrium within the time interval considered, i.e., as long as diffusion remains the determining step, the backward and the forward curves are strictly superposable.⁽⁶⁰⁾ However, there is a quite different situation as soon as charge transfer or a chemical reaction interferes in the rate-determining step. For example, in the case of a "quasi-reversible" charge transfer, the voltammogram exhibits a hysteresis which is greater the slower the transfer and the faster the sweep (Figure 15).

4.1.2. Multi-step Heterogeneous Reactions

With this kind of investigation, it is generally necessary to integrate numerically the non-linear differential equations which describe the interface behavior.⁽⁶²⁻⁶⁵⁾ For example, the relaxation of two co-adsorbed electroactive species has been simulated by Conway *et al.*⁽⁶⁶⁾

Two anodic electrochemical reactions are considered, a slow one and a fast one, the latter involving a chemisorbed hydrogen atom, i.e.:



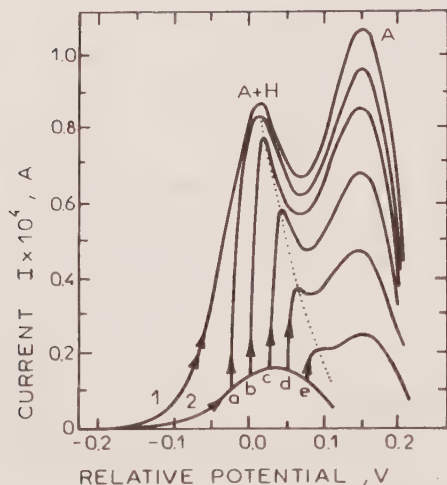


Figure 16. Calculated current-potential curves from the equation system (141-142) for a process involving two species A and H at different sweep rates [from Reference (66)]. $k_1 = k_{-1} = 10 \text{ s}^{-1}$; $k_2 = k_{-2} = 0.1 \text{ s}^{-1}$. Curve 1: $\nu_1 = 0.1 \text{ V s}^{-1}$, curve 2: $\nu_2 = 0.01 \text{ V s}^{-1}$. At points a, b, c, d, and e the sweep rate is changed from ν_1 into ν_2 [see Table 1(c)].

where B denotes an adsorbed electroactive molecule (a nitrile, for example), coming from the solution bulk through a non-electrochemical chemisorption step, and which can be reduced into an adsorbed species BH through an electron transfer step; BH can be re-oxidized into B at the electrode surface through reaction (Ib).

The kinetic equations describing the behavior of this reaction mechanism can be written as:

$$\frac{d\theta_H}{dt} = -k_1^0 \theta_H \exp(\alpha FE/RT) + k_1'^0 (1 - \theta_H) \exp[-(1 - \alpha)FE/RT] C_{H^+} \quad (141)$$

$$\frac{d\theta_{BH}}{dt} = -k_2^0 \theta_{BH} \exp(\alpha FE/RT) + k_2'^0 \theta_B \exp[-(1 - \alpha)FE/RT] C_{H^+} \quad (142)$$

θ_H and θ_{BH} are the coverage fractions of the surface by H^+ and BH, respectively. Integrating with a Runge-Kutta method allows one to simulate the response to a single ramp, a double scan ramp [Table 1(c)], or a cyclic signal (Figure 16).

In using a double scan ramp, one can readily ascertain the relaxation of two co-adsorbed species by doing only one experiment.

The advantage of this method in revealing adsorption-desorption processes can be shown on another example. It is well known that, at the corrosion potential in sulfuric acid medium, the current-potential curve of iron presents a hysteresis when a forward-backward potential sweep is applied.⁽⁶⁷⁾ This phenomenon is enhanced when a corrosion inhibitor, such as 2-butyne-1,4-diol, is added to the medium (Figure 17). It was long believed that this phenomenon was due to spurious processes caused by impurities in the solution. However, it has been shown recently that this hysteresis can be interpreted

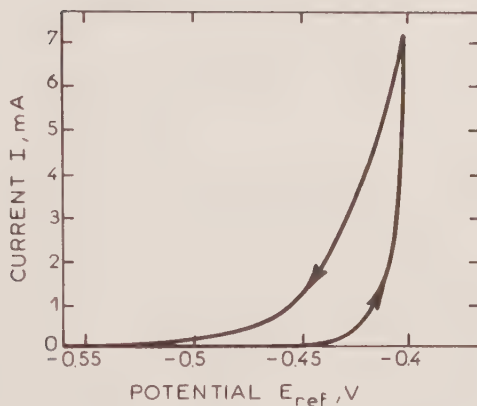
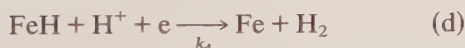


Figure 17. Anodic polarization curves (forward and backward potential sweeps): iron, $1\text{ M H}_2\text{SO}_4 + 10^{-3}\text{ M 2-butyne-1,4-diol}$, with $\nu = 3.3\text{ mV s}^{-1}$ [from Reference (68)].

in terms of an adsorption-desorption process of adsorbed hydrogen. As a matter of fact, the following simplified reaction mechanism is generally accepted to be valid at the corrosion potential of iron in sulfuric acid medium ($\text{pH} = 0$).



If θ_1 and θ_2 denote the coverage fractions of FeOH and FeH, respectively, and if $k_i = k_i^0 \exp(b_i E)$, the interface behavior can be described by the following differential equations:

$$\beta_1 \frac{d\theta_1}{dt} = (1 - \theta_1 - \theta_2)k_1 - k_{-1}\theta_1 - k_2\theta_1 \quad (143)$$

$$\beta_2 \frac{d\theta_2}{dt} = (1 - \theta_1 - \theta_2)k_3 - k_{-3}\theta_2 - k_4\theta_2 \quad (144)$$

$$I_F = FA[(1 - \theta_1 - \theta_2)k_1 - k_{-1}\theta_1 + k_2\theta_1 - (1 - \theta_1 - \theta_2)k_3 + k_{-3}\theta_2 - k_4\theta_2] \quad (145)$$

Taking account of the double-layer capacity and the electrolyte resistance (see Figure 3), one can integrate these equations using a predictor-corrector method. The simulated polarization curve is in good agreement with the experimental one.

4.1.3. Other Applications of Ramp Techniques

It has been shown that a linear variation of the potential of an electrode is the basis of the well-known linear voltammetry method, but a potential sweep can also be used to other ends.

4.1.3.1. Plotting of Polarization Curves

Potential ramps can be used for plotting steady state current-potential curves. As a matter of fact, when the sweep rate tends to zero, the voltammogram becomes identical to a steady state plot. However, when solid, soluble electrodes are used (dissolution, passivation), the steady state or non-steady state character of these plots is far from being always obvious.

4.1.3.2. Measurement of the Polarization Resistance

The polarization resistance, which is the limit of the impedance at low frequencies [$R_p = \lim_{\omega \rightarrow 0} Z(\omega)$], is equal to the reciprocal of the slope of the current-potential curve

$$R_p = dE_{\text{ref}}/dI_F \quad (146)$$

For corroding systems the value of this resistance at the rest potential is generally related to the resistance of the sample to galvanic corrosion.⁽⁶⁹⁾

If it is assumed that the electrode impedance can be simplified into the scheme depicted in Figure 3, where $Z(\omega) \rightarrow R_p$ when $\omega \rightarrow 0$, then the equations describing the behavior of the interface are:

$$I = I_F + C_d \frac{dE}{dt} \quad (147)$$

and

$$I = \frac{E_{\text{ref}} - E}{R_e} \quad (148)$$

Consequently, the equation describing the variation of the overpotential at the interface is:

$$\frac{dE}{dt} = -\frac{E}{C_d} \left(\frac{1}{R_e} + \frac{1}{R_p} \right) + \frac{E_{\text{ref}}}{R_e C_d} \quad (149)$$

When using a signal like the one depicted in Table 1(b), i.e., with

$$\begin{aligned} 0 \leq t \leq t_1 \quad E_{\text{ref}}(t) &= \frac{E_{02} - E_{01}}{t_1} t + E_{01} \\ t_1 \leq t \leq 2t_1 \quad E_{\text{ref}}(t) &= -\frac{E_{02} - E_{01}}{t_1} t + 2E_{02} - E_{01} \end{aligned} \quad (150)$$

Eq. (149) can be integrated analytically thus giving:

$$E(t) = At + B - (Aa + B) \exp[-\alpha(t - a)] + D \exp[-\alpha(t - a)] \quad (151)$$

with

$$\alpha = \frac{1}{C_d} \left[\frac{1}{R_e} + \frac{1}{R_p} \right]; \quad A = \frac{\beta}{\alpha}; \quad \beta = \frac{E_{02} - E_{01}}{R_e C_d t_1};$$

$$B = \frac{1}{\alpha} \left(\gamma - \frac{\beta}{\alpha} \right); \quad \gamma = \frac{E_{01}}{R_e C_d}$$
(152)

the initial conditions being:

$$t = a = 0; \quad E_{\text{ref}} = E_{01}; \quad D = \frac{R_p}{R_e + R_p} E_{01}$$

Figure 18 shows that a rapid increase of the current (branch AB) is obtained, with a time constant $1/\alpha \approx R_e C_d$. Beyond this steep rise, the current increases according to the linear law:

$$I_{\text{lin}}(t) = \frac{E_{\text{ref}} - (At + B)}{R_e}$$
(153)

Now

$$\frac{dE_{\text{ref}}}{dI_{\text{lin}}} = \frac{dE_{\text{ref}}}{dt} \cdot \frac{dt}{dI_{\text{lin}}}$$
(154)

By Eq. (150) we have:

$$\frac{dE_{\text{ref}}}{dt} = \frac{E_{02} - E_{01}}{t_1}$$
(155)

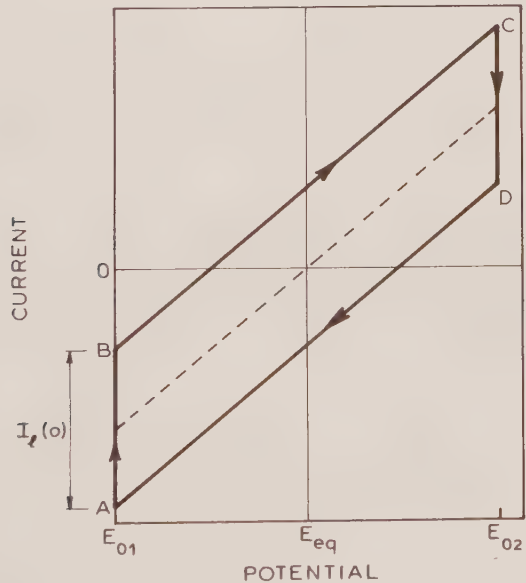


Figure 18. Measurement of the polarization resistance using a ramp signal [see Table 1(b)]. R_p is related to the slope of branch BC through Eq. (156), and $I_t(0)$ to C_d through Eq. (159).

and by Eq. (153):

$$\frac{dI_{\text{lin}}}{dt} = \frac{1}{R_e} \frac{dE_{\text{ref}}}{dt} \left(1 - \frac{1}{R_e C_d} \frac{R_e R_p}{R_p + R_e} C_d \right) = \frac{dE_{\text{ref}}}{dt} \cdot \frac{1}{R_p + R_e} \quad (156)$$

Consequently

$$\frac{dE_{\text{ref}}}{dI_{\text{lin}}} = R_p + R_e \quad (157)$$

Moreover

$$I_{\text{lin}}(0) = \frac{1}{R_e} \left[E_{01} - \frac{R_p R_e}{R_p + R_e} C_d \left(\frac{E_{01}}{R_e C_d} - \frac{E_{02} - E_{01}}{t_1} \frac{R_p}{R_p + R_e} \right) \right] \quad (158)$$

and if one assumes that $R_p \gg R_e$, then

$$I_{\text{lin}}(0) = C_d \frac{E_{02} - E_{01}}{t_1} \quad (159)$$

Equation (159) corresponds to the charging current of the double-layer capacity $C_d(dE/dt)$, and therefrom R_p and C_d can be readily determined.

We must note that this derivation is only valid when it is assumed that the equivalent circuit of the interface is a R-C device (like Figure 3 with $Z = R_p$). If the equivalent circuit is more complicated, R_p is not so easy to obtain and the method is much less attractive.

4.2. Step Techniques

In such techniques, a step-signal is applied either to the potential or to the current. In the first case, the current (chronoamperometry) or the charge (chronocoulometry) and, in the second case, the potential (chronopotentiometry) is recorded as a function of time.⁽⁷¹⁾

4.2.1. Potential step methods

The potential step method was proposed in 1955 by Gerisher and Vielstich⁽⁷²⁾ and was modified afterwards. However, this method requires devices (particularly a potentiostat) which exhibit a very short rise-time (less than 1 μ s).

4.2.1.1. Single Potential Step Method [Table 1(d)]

In Section 2.3.2 we have seen that in the case of a diffusion-controlled electron transfer, the current response to a single potential step is, by virtue of Eq. (59) when λ is given by Eq. (58):

$$I_F(t) = nFA(k_f c_O^* - k_b c_R^*) \zeta(\lambda t^{1/2}) \quad (160)$$

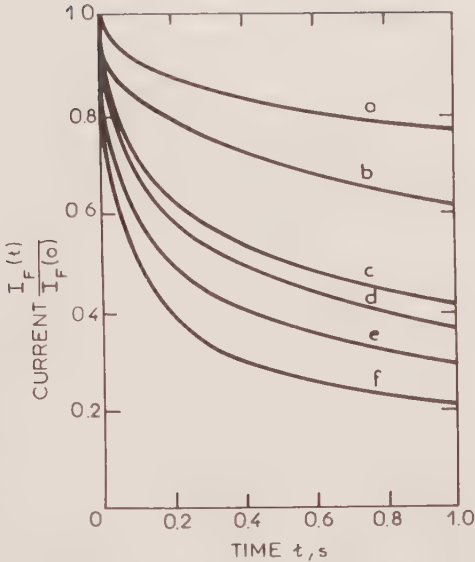


Figure 19. Simulated current ratio $I_F(t)/I_F(0) = \zeta(t)$ as a function of time for an electron charge transfer controlled by diffusion for an anodic voltage pulse. Values used: $\eta = 80 \text{ mV}$; $I_0 = 1 \text{ mA cm}^{-2}$; $\alpha = 0.5$; $D_1 = D_2 = 1.5 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$; $c_O^* = 0.1 \text{ M}$; varied parameter c_R^* ; curve a: $c_R^* = 5 \cdot 10^{-2} \text{ M}$; b: $2.5 \cdot 10^{-2}$; c: $1.2 \cdot 10^{-2}$; d: 10^{-2} ; e: $7.5 \cdot 10^{-3}$; f: $5 \cdot 10^{-3}$ [from Reference (73)].

which can be rewritten as:

$$I_F(t) = I_D \zeta(\lambda t^{1/2}) \tag{161}$$

with

$$\zeta(\lambda t^{1/2}) = \exp(\lambda^2 t) \operatorname{erfc}(\lambda t^{1/2}) \tag{162}$$

For example, Figure 19 shows $I_F(t)$ transients digitally simulated under various conditions.

It must be noted that Eq. (160) cannot be used at long times because of free convection (finite thickness of δ_N). Moreover this relation is often considered as too complicated to be applied directly, and a certain number of approximations have therefore to be made.

(a) If the amplitude of the potential step is such that $\eta = E - E_{eq} \ll RT/nF$ (i.e., from 2 to 5 mV), the Tafel exponentials can be expanded in a series in Eq. (160) and, by considering only the first two terms, this yields:

$$I_F = I_0 \frac{nF\eta}{RT} \zeta(\lambda t^{1/2}) \tag{163}$$

That is, by Eq. (72):

$$I_F = (1/R_{ct}) \eta \zeta(\lambda t^{1/2}) \tag{164}$$

and

$$\lambda = I_0 \Xi \tag{165}$$

with

$$\Xi = \frac{1}{nFA} \left(\frac{1}{c_O^* D_O^{1/2}} + \frac{1}{c_R^* D_R^{1/2}} \right) \quad (166)$$

(b) It is assumed that the duration of the potential variation is sufficiently short so that:

$$\lambda t^{1/2} \ll 1 \quad (167)$$

then

$$\exp(\lambda^2 t) \simeq 1 \quad (168)$$

and

$$\operatorname{erfc}(\lambda t^{1/2}) \simeq 1 - \frac{2\lambda t^{1/2}}{\pi^{1/2}} \quad (169)$$

Hence:

$$I_F = (1/R_{ct}) \eta \left(1 - \frac{2\lambda}{\pi^{1/2}} \cdot t^{1/2} \right) \quad (170)$$

Consequently, it is sufficient to plot the current measured versus $t^{1/2}$. By extrapolating to zero the straight line thus obtained, R_{ct} and I_0 can be determined and λ deduced from its slope (Figure 20a). However, as can be seen in Figure 20a, this extrapolation is not very easy.

This method was modified by Vielstich and Delahay⁽⁷⁵⁾ in order to simplify the experimental device and to take account of the instantaneous value of the ohmic drop during the response, using the following equation:

$$\eta + IR_e = E_{ref} \quad (171)$$

In this case, if only small potential steps are used (2 to 5 mV) and for $\lambda_1 t^{1/2} \ll 1$ one has:

$$I_F = I_0 \frac{nF}{RT} \eta \frac{1}{r+1} \left(1 - \frac{2\lambda_1}{\pi^{1/2}} t^{1/2} \right) \quad (172)$$

with

$$r = I_0 R_e \frac{nF}{RT} \quad (173)$$

and

$$\lambda_1 = \frac{I_0 \Theta}{r+1} \quad (174)$$

However, this method which uses only the extrapolation to zero of the current recorded, has been thought of as being too restrictive and even

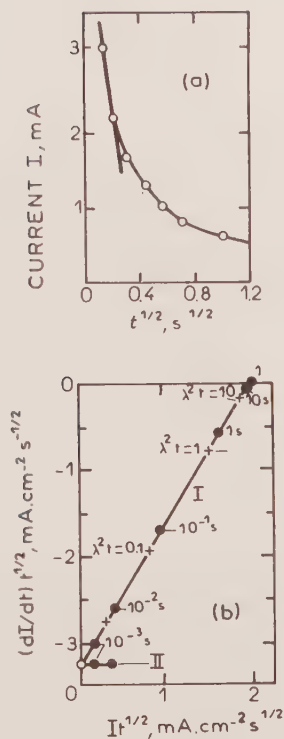


Figure 20. Two different treatments of the current response to a potential step. Curve a: Experimental plot of I vs. $t^{1/2}$ in the case of the discharge of $2.1 \cdot 10^{-3} M$ zinc in $1 M$ sodium perchlorate on a zinc amalgam for $\eta = -0.06 V$ at $0^\circ C$. Kinetic parameters derived therefrom: $I_0 = 2.1 \text{ mA cm}^{-2}$; $\alpha = 0.7$ [from Reference (74)]. Curve b: Theoretical $(dI/dt)t^{1/2}$ vs. $It^{1/2}$ plots corresponding to the model of a diffusion-controlled electron transfer (I) and its approximation for small t (II). The same parameter values are used as for curve d in Figure 19 [from Reference (73)].

dangerous in certain cases, by some authors who proposed plotting $(dI_F/dt)t^{1/2}$ as a function of $I_F t^{1/2}$.⁽⁷³⁾ A straight line is thus obtained over a very wide time range whose slope is λ^2 (Figure 20b) and which intersects the axes at:

$$\left(\frac{dI_F}{dt} t^{1/2}\right)_0 = -\frac{I_D}{\pi^{1/2}} \lambda \quad \text{and} \quad (I_F t^{1/2})_0 = \frac{I_D}{\lambda \pi^{1/2}} \quad (175)$$

Thus parameters α , I_0 and k_i are determined more accurately, since the whole $I_F(t)$ curve is taken into account.

It is to be noted that the extrapolation to zero of the experimental $I-t^{1/2}$ curve can be difficult because of the charging current of the double-layer capacity C_d . As a matter of fact, the overall current I is equal, by Eq. (14), to:

$$I = I_F + C_d \frac{d\eta}{dt} \quad (176)$$

if C_d is assumed not to vary within the potential range explored.

During the charging time of C_d , it is difficult to determine the faradaic current. In order to get around this difficulty, it has been proposed to employ a short pre-impulse [Table 1(e)] in order to charge the double-layer capacity very rapidly.

However, despite these various modifications, the method turned out to be very difficult to apply when reaction mechanisms involving chemical reactions before the electron transfer are studied.

4.2.1.2. Double Potential Step Method

In order to investigate complicated reaction mechanisms, Schwarz and Shain proposed in 1965⁽⁷⁶⁾ to use a double potential step and analyze the current response (chronoamperometry). Eventually, Christie⁽⁷⁷⁾ recommended analyzing the variation of the charge passing through the electrode by integrating the current (chronocoulometry). The principle of this last method will be described below.

Let us consider, for example, the case of a reversible electron transfer having an equilibrium potential E_{eq} [Table 1(g)]. A potential E_1 is imposed for a period of time τ to the system such that the only reaction is the cathodic one, i.e.,



After the time τ is elapsed, another potential E_2 is imposed such that the only reaction is the anodic one, i.e.,



In addition these potentials must satisfy the condition that the reaction rates in the anodic and cathodic domains are such that the limiting diffusion current is always reached, i.e.,

$$c_0(0, 0 < t \leq \tau) = 0 \quad \text{and} \quad c_R(0, t \geq \tau) = 0 \quad (177)$$

In that case, we will have of course $E_1 > E_{eq} > E_2$.

Since the possible chemical reactions are not affected by the potential, they occur without interruption.

In the case of a pure electron transfer (i.e., without chemical reaction), if we assume that $c_R^* = 0$, we have by Eq. (62):

$$\mathcal{L}I_F(s) = nFA(D_R s)^{1/2} \mathcal{L}c_R(0, s) \quad (178)$$

Since:

$$Q(t) = \int_0^t I_F(\theta) d\theta \quad (179)$$

and

$$\mathcal{L}Q(s) = \mathcal{L}I_F(s)/s \quad (180)$$

it can be written that

$$\mathcal{L}Q(s) = [nFAD_R^{1/2} \mathcal{L}c_R(0, s)]/s^{1/2} \quad (181)$$

and

$$Q(t) = \frac{nFAD_R^{1/2}}{\pi^{1/2}} \int_0^t \frac{c_R(0, \theta)}{(t - \theta)^{1/2}} d\theta \quad (182)$$

Since it is assumed that $c_R(0, t \geq \tau) = 0$, then

$$Q(t \leq \tau) = \frac{nFAD_R^{1/2}}{\pi^{1/2}} \int_0^t \frac{c_R(0, \theta)}{(t - \theta)^{1/2}} d\theta \quad (183)$$

and

$$Q(t > \tau) = \frac{nFAD_R^{1/2}}{\pi^{1/2}} \int_0^\tau \frac{c_R(0, \theta)}{(t - \theta)^{1/2}} d\theta \quad (184)$$

Since $c_O(0, t \leq \tau) = 0$, one has by virtue of Eq. (65):

$$c_R(0, t \leq \tau) = (D_O/D_R)^{1/2} \cdot c_O^* \quad (185)$$

By integrating

$$Q(t \leq \tau) = \frac{2nFAD_O^{1/2} c_O^*}{\pi^{1/2}} t^{1/2} \quad (186)$$

$$Q(t > \tau) = \frac{2nFAD_O^{1/2} c_O^*}{\pi^{1/2}} [t^{1/2} - (t - \tau)^{1/2}] \quad (187)$$

If we set:

$$Q_c = \frac{2nFAD_O^{1/2} c_O^*}{\pi^{1/2}} \tau^{1/2} \quad (188)$$

we have:

$$\frac{Q(t \leq \tau)}{Q_c} = \left(\frac{t}{\tau}\right)^{1/2}; \quad \frac{Q(t > \tau)}{Q_c} = \left(\frac{t}{\tau}\right)^{1/2} - \left(\frac{t}{\tau} - 1\right)^{1/2} \quad (189)$$

Relation (189) is plotted in Figure 21.

In general, one defines a second arbitrary characteristic time ($t = 2\tau$ for example), which leads to:

$$\left| \frac{Q_b}{Q_f} \right| = \left| \frac{Q(2\tau) - Q(\tau)}{Q(\tau)} \right| = 2 - 2^{1/2} = 0.5858 \quad (190)$$

which can be interpreted in terms of the ratio between the charge Q_b passing through the interface owing to the backward reaction from $t = \tau$ up to $t = 2\tau$ divided by the charge Q_f passed during the forward reaction. Q_b/Q_f is the characteristic ratio for double potential step coulometry. A deviation from the value of 0.5858 indicates that the system studied is not as simple as was assumed here and that processes other than electron transfer occur simultaneously.

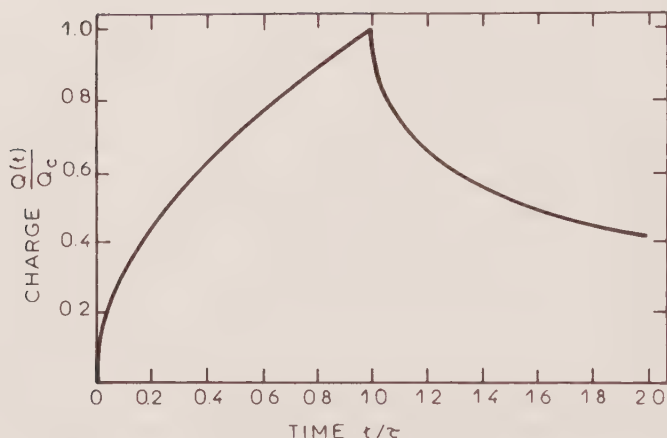


Figure 21. Double potential step method. $Q(t)/Q_c$ vs. t/τ for a pure electron transfer, calculated from Eq. (189) [from Reference (77)].

In the case of a chemical reaction preceding or following the electron transfer, the problem can be solved in certain cases, and another parameter Q_b/Q_f can be defined as above [Eq. (190)]. If the chemical reaction follows the electron transfer, this parameter can be plotted as a function of $(k\tau)^{1/2}$ where k is the rate constant of the chemical reaction (Figure 22). Of course, at $t = 0$ we find again the value 0.5858 which characterizes pure transfer.⁽⁷⁸⁾

The double potential step method has been applied to various cases of chemical reactions and to several simultaneous electron transfers. This method has been particularly studied by Holub and Weber⁽⁷⁹⁾ who specified its limitations using Green's method.

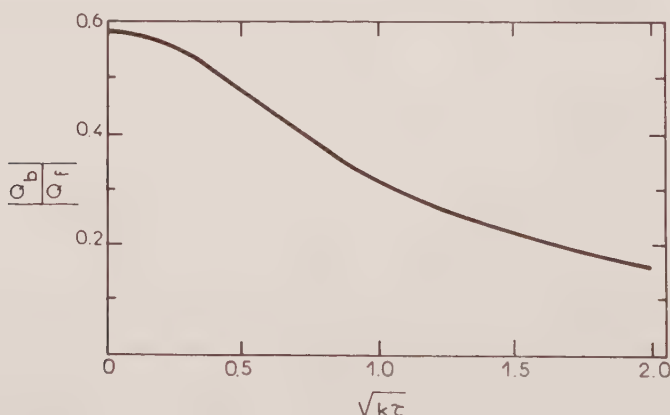


Figure 22. Double potential step method. $|Q_b/Q_f|$ vs. $(k\tau)^{1/2}$ for a chemical reaction (rate constant k) following the charge transfer [from Reference (77)].

4.2.1.3. Cyclic Potential Step Method

The double potential step method has been extended to three steps, then to a series of steps. Thus, in 1960, Smit and Wijnen⁽⁸⁰⁾ proposed that the potential be varied in a cyclic manner [Table 1(g)].

Thus, for the first half-period, the boundary conditions are identical to those of the single potential step method. Subsequently, the boundary conditions vary with time:

$$c_O(z, 0) = c_O^* \quad \text{at } t = 0$$

then by Eq. (160):

$$I_1 = nFA[k_f(E_1)c_O^* - k_b(E_1)c_R^*]\zeta[\lambda(E_1)t^{1/2}] \quad (191)$$

At $t = \tau_1$, at the beginning of the second half-period, $c_O(z, \tau_1)$ can be written as:

$$c_O(z, \tau_1) = c_O^* - \frac{k_f(E_1)c_O^* - k_b(E_1)c_R^*}{\lambda(E_1)D_O^{1/2}} \left\{ \operatorname{erfc} \left[\frac{z}{2(D_O\tau_1)^{1/2}} \right] - \exp \left[\frac{\lambda(E_1)z}{D_O^{1/2}} + \lambda^2(E_1)\tau_1 \right] \operatorname{erfc} \left[\frac{z}{2(D_O\tau_1)^{1/2}} + \lambda(E_1)\tau_1^{1/2} \right] \right\} \quad (192)$$

Smit and Wijnen gave a solution of Fick's equations only in the case where $\lambda(E_1) = \lambda(E_2)$, i.e.,

$$\frac{k_f(E_1)}{D_O^{1/2}} + \frac{k_b(E_1)}{D_R^{1/2}} = \frac{k_f(E_2)}{D_O^{1/2}} + \frac{k_b(E_2)}{D_R^{1/2}} \quad (193)$$

The expression giving the current at all the periods, for an infinite number of periods such as $\tau_1 = \tau_2 = \tau$, can be deduced if we set $t/\tau = h$ and $S = \lambda t^{1/2}$.

In this case we have $|I_{2i+1}| = -|I_{2i}| = |I|$ (symmetry of current of two consecutive half-periods) provided that $i \rightarrow \infty$ and then

$$|I(h)| = nFA\{c_O^*[k_f(E_1) - k_f(E_2)] - c_R^*[k_b(E_1) - k_b(E_2)]\}L(S, h) \quad (194)$$

with

$$L(S, h) = \sum_{p=0}^{\infty} \{\zeta[S(p+h)^{1/2}] - \zeta[S(p+h+1/2)^{1/2}]\} \quad (195)$$

and $\zeta(S)$ given by Eq. (162).

This function has been calculated by Smit and Wijnen (Figure 23).

Consequently, from an experimental standpoint, one has to fulfill the two following requirements:

- (i) It is necessary to obtain experimentally $\lambda(E_1) = \lambda(E_2)$ in order to adjust the symmetry of the current, by varying E_2 at a given E_1 .
- (ii) It is necessary to reach one of the values of S at which $L(S, h)$ has been calculated, by varying the frequency of the steps.

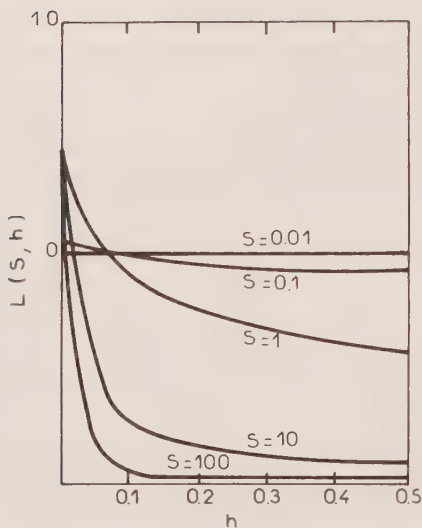


Figure 23. Cyclic potential step method. $L(S, h)$ as a function of $h = t/\tau$ at different values of $S = \lambda t^{1/2}$ [see Eq. (195)] [from Reference (80)].

The current is observed with an oscilloscope, but it is not always easy to establish the symmetry of the current for the first and second half-periods.

A general equation for the current response to a signal formed by steps of any amplitude and time values [Table 1(h)] was given by Rifkin and Evans⁽⁸¹⁾ on the basis of Schwarz and Shain's investigations.⁽⁷⁶⁾ For $\tau_j < t_j < \tau_{j+1}$ they assumed that both Frick's law and the Nernst relation are valid at the electrode, i.e., by Eq. (43)

$$c_O(0, t)/c_R(0, t) = \gamma_j = \exp[(nF/RT)(E_j - E^\circ)] \quad (196)$$

hence

$$I_F(t) = \frac{nFAD_O^{1/2}c_O^*}{\pi^{1/2}} \sum_{j=1}^m \frac{\Delta\Psi_j}{(t - \tau_j)^{1/2}} \quad (197)$$

where m is the number of potential changes preceding time t , and

$$\Delta\Psi_j = \frac{\gamma_{j-1}[\gamma_0 + (D_R/D_O)^{1/2}]}{\gamma_0[\gamma_{j-1} + (D_R/D_O)^{1/2}]} - \frac{\gamma_j[\gamma_0 + (D_R/D_O)^{1/2}]}{\gamma_0[\gamma_j + (D_R/D_O)^{1/2}]} \quad (198)$$

4.2.1.4. Application of the Convolution Procedure to the Potential Step Method

As was seen above, the analytical expressions of the $I(t)$ and $Q(t)$ variations are highly complicated. Therefore certain authors have proposed that, instead of using the values at long and short times at which the relations are linear, all the data be considered as functions of time in order to determine the parameters through a non-linear regression.^(82,83)

However, it appears that a simpler method is to use the convolution (or semi-integral) properties which do not depend on the shape of the excitation signal (see Section 2.3.1.2).

For a redox process, it can be written, by Eqs. (63) and (64), that:

$$c_O(0, t) = c_O^* - \frac{\hat{I}_F(t)}{nFAD_O^{1/2}} \quad (199)$$

$$c_R(0, t) = c_R^* + \frac{\hat{I}_F(t)}{nFAD_R^{1/2}} \quad (200)$$

where the convoluted current $\hat{I}_F(t)$ is given by Eq. (136).

Thus by Eq. (31) we can write:

$$I_F(t) = nFA(k_f c_O^* - k_b c_R^*) - \left(\frac{k_f}{D_O^{1/2}} + \frac{k_b}{D_R^{1/2}} \right) \hat{I}(t) \quad (201)$$

That is

$$I_F(t) = I_D - \lambda \hat{I}_F(t) \quad (202)$$

I_D and λ can be determined (Figure 24) from the straight line $I_F = f(\hat{I}_F)$.

For a double potential step, we obtain by differentiating Eqs. (186) and (187):

$$I_F(t) = \begin{cases} \frac{nFAc_O^* D_O^{1/2}}{\pi^{1/2}} \cdot \frac{1}{t^{1/2}} & \text{for } 0 < t \leq \tau \quad (203) \\ \frac{nFAc_O^* D_O^{1/2}}{\pi^{1/2}} \left[\frac{1}{t^{1/2}} - \frac{1}{(t - \tau)^{1/2}} \right] & \text{for } t > \tau \quad (204) \end{cases}$$

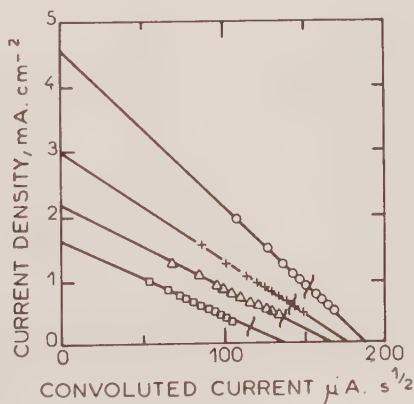


Figure 24. Faradaic current density vs. its convoluted current for 1 mM $\text{Eu}(\text{ClO}_4)_3$ in 0.1 M NaNCS, 0.01 M LaCl_3 [from Reference (84)].
 $\square$ $E = -0.65$ V; $\triangle$ $E = -0.67$ V; $+$ $E = -0.69$ V; $\circ$ $E = -0.71$ V.

hence

$$\frac{\hat{I}_F(t)}{nFAC_O^*D_O^{1/2}} = \begin{cases} \frac{1}{\pi} \int_0^t \frac{d\theta}{[\theta(t-\theta)]^{1/2}} = 1 & \text{for } 0 < t \leq \tau \\ 1 - \left\{ \frac{1}{\pi} \int_\tau^t \frac{d\theta}{[(\theta-\tau)(t-\theta)]^{1/2}} \right\} = 0 & \text{for } t > \tau \end{cases} \quad (205)$$

This curve is altered if a homogeneous chemical reaction takes place as depicted in Figure 25. For example, for an ECE (electrochemical-chemical-electrochemical) mechanism, one has⁽⁸⁵⁾ for a chemical reaction of rate constant k_1 :

$$I_F(t) = \frac{nFAC_R^*D_R^{1/2}}{(\pi t)^{1/2}} [2 - \exp(-k_1 t)] \quad \text{for } 0 < t \leq \tau \quad (207)$$

Inserting this value in Eq. (136), an analytical solution for $\hat{I}(t)$ can be obtained:

$$\hat{I}_F(t) = \frac{nFAC_R^*D_R^{1/2}}{\pi^{1/2}} \int_0^t \frac{[2 - \exp(-k_1 \theta)] d\theta}{[\theta(t-\theta)]^{1/2}} \quad (208)$$

hence

$$\hat{I}_F(t) = nFAC_R^*D_R^{1/2} [2 - I_0(k_1 t/2) \exp(-k_1 t/2)]$$

where I_0 is the zero-order modified Bessel function of the first kind. The characteristic parameters are defined here as $I_F(2\tau)/I_F(\tau)$ and $Q(2\tau)/Q(\tau)$.

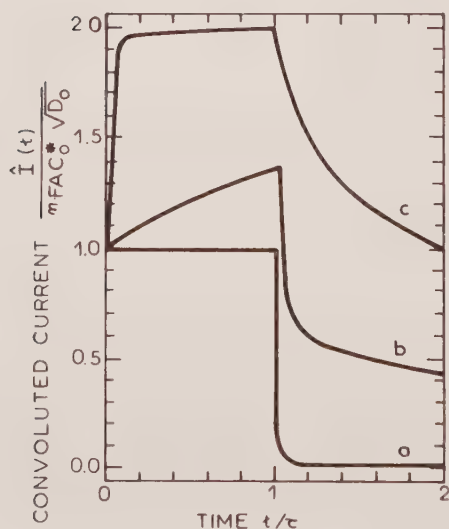


Figure 25. Simulated results of double potential step method studied by convolution procedure for an ECE mechanism. k_1 is the rate constant of the chemical reaction. Curve a: $k_1\tau = 0.001$; curve b: $k_1\tau = 1$; curve c: high value of $k_1\tau$ [from Reference (85)].

4.2.2. Current Step Methods

4.2.2.1. Single Current Step Method

A current step is imposed starting from the rest-potential E_{eq} at which no current passes through the electrode [Table 1(i)]. The variation of the overvoltage $\eta = E - E_{eq}$ is recorded.

Now, we have:

$$I_F(t > 0) = nFAD_O \frac{\partial c_O(0, t)}{\partial z} = \text{constant} = I_A \quad (209)$$

The entire expression for the concentrations as functions of the time and distance can be obtained,⁽⁸⁶⁾ but since we are interested in the values of the concentrations at $z = 0$ only, we can directly integrate Eqs. (63) and (64) for $I_F(t) = I_A$. Hence

$$c_O(0, t) = c_O^* - \frac{2I_A}{nFA(D_O\pi)^{1/2}} t^{1/2} \quad (210)$$

$$c_R(0, t) = c_R^* + \frac{2I_A}{nFA(D_R\pi)^{1/2}} t^{1/2} \quad (211)$$

Note that these expressions lead to infinite concentrations (either positive or negative) when $t \rightarrow \infty$. This arises directly from the acceptance of boundary conditions at an infinite distance from the interface. Therefore, caution must be exercised in using these relations at long times.

Transferring the values of $c_O(0, t)$ and $c_R(0, t)$ to Eq. (42) giving the current, a complicated expression is obtained. However, if the experimental conditions are such that the resulting overpotential does not vary too much, i.e., if $\eta \ll RT/nF$ ($\eta = 2$ to 5 mV) one has^(2,75,87)

$$I_F(t) = I_0 \left[\frac{c_O(0, t)}{c_O^*} - \frac{c_R(0, t)}{c_R^*} - \frac{nF}{RT} \eta \right] \quad (212)$$

hence

$$\eta = -\frac{RT}{nF} I_A \left\{ \left[\frac{2}{nF\pi^{1/2}} \left(\frac{1}{c_O^* D_O^{1/2}} + \frac{1}{c_R^* D_R^{1/2}} \right) \right] t^{1/2} + \frac{1}{I_0} \right\} \quad (213)$$

That is

$$\eta = -\frac{RT}{nF} I_A \left(\frac{2\Theta}{\pi^{1/2}} t^{1/2} + \frac{1}{I_0} \right) \quad (214)$$

with Θ given by Eq. (166).

Under such linear conditions, the potential [Eq. (170)] and the current [Eq. (214)] step methods give the $t^{1/2}$ -dependence for the current and for the potential, respectively. Similarly, under the same conditions a $\omega^{1/2}$ -dependence

has been found for the Warburg impedance [Eq. (79)]. It can be concluded therefrom that a time dependence in $t^{1/2}$ and a frequency dependence in $\omega^{1/2}$ are characteristic of diffusion-controlled processes.

4.2.2.2. Cyclic Current Step Method

In 1960 Wijnen and Smit⁽⁸⁸⁾ proposed that a series of current steps be used [Table 1(j)]. The solution of Fick's law is here more complicated and can be performed only when the current charging the double layer is disregarded. A solution is possible if the charge passing during each half-period is the same, i.e.,

$$I_1\tau_1 = -I_2\tau_2 \quad (215)$$

where I_1 , I_2 and τ_1 , τ_2 are the current steps imposed and the durations of the two consecutive half-periods, respectively.

After about a hundred periods, one observes a cyclic state, and the expressions for the concentrations at the electrode surface are, if $\tau = \tau_1 + \tau_2$: at odd half-periods, $t = N\tau + t'$

$$c_O(0, t') = c_O^* - (I_1 - I_2) \frac{2L(t')\tau^{1/2}}{nF(\pi D_O)^{1/2}} \quad (216)$$

and at even half-periods, $t = N\tau + \tau_1 + t''$

$$c_O(0, t'') = c_O^* - (I_1 - I_2) \frac{2L(t'')\tau^{1/2}}{nF(\pi D_O)^{1/2}} \quad (217)$$

where $L(t)$ is a tabulated function given in Figure 26.

When $\eta \ll RT/nF$, one has by Eq. (212):

$$\eta = \frac{RT}{nF} \left(\frac{I_F}{I_0} - \frac{c_O}{c_O^*} + \frac{c_R}{c_R^*} \right) \quad (218)$$

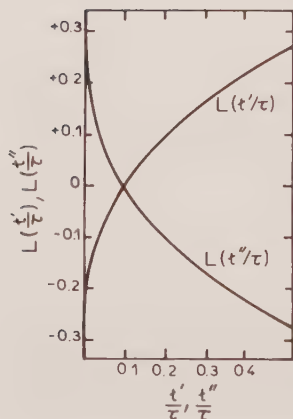


Figure 26. $L(t'/\tau)$ and $L(t''/\tau)$ as a function of t'/τ and t''/τ , respectively [from Reference (88)].

If the amount of charge passing in the two half-periods is equal, then,

$$\eta(t') = \frac{RT}{nF} \left[\frac{I_1}{I_0} + \frac{2(I_1 - I_2)}{\pi^{1/2}} \Theta \tau^{1/2} L(t') \right] \quad (219)$$

and

$$\eta(t'') = \frac{RT}{nF} \left[\frac{I_2}{I_0} + \frac{2(I_1 - I_2)}{\pi^{1/2}} \Theta \tau^{1/2} L(t'') \right] \quad (220)$$

where Θ is given by Eq. (166).

4.2.2.3. Influence of the Charging Current of the Double-layer Capacity

The applicability of the current step method is limited by the fact that at very short times the double layer charging current prevails, and therefore by the fact that the equations established previously are only applicable at times $t > 10^{-5}$ s. As the double-layer charging current is generally difficult to calculate, it is only in the case of low-amplitude potential variations that the calculations can be carried out.

4.2.2.3.1. Influence of the Double-layer Charging Current. If the charging current is taken into account in the boundary conditions, then the total current I flowing through the electrode is:

$$I = C_d \frac{d\eta}{dt} + nFA D_O \frac{\partial c_O}{\partial z}(0, t) = I_A = \text{constant} \quad (221)$$

Solving Fick's law is highly complicated in the general case. A solution was given by Berzins and Delahay⁽⁸⁹⁾ for $\eta \ll RT/nF$

$$\eta = \frac{RT}{nF} I_A \left(\frac{2\Xi}{\pi^{1/2}} t^{1/2} + \frac{1}{I_0} - \frac{RT\Xi^2}{nF} C_d \right) \quad (222)$$

Here again, the curve $\eta = f(t^{1/2})$ is plotted for $t > 10^{-5}$ s when the double-layer charging current becomes negligible. The slope of the corresponding straight line is:

$$a = \frac{2RT\Xi}{nF\pi^{1/2}} I_A \quad (223)$$

A characteristic time τ is defined such that:

$$\eta_\tau = \frac{RT}{nF} \frac{I_A}{I_0} \quad (224)$$

where the concentration polarization term in Eq. (222) is equal to the term related to the double-layer charge, i.e.,

$$\frac{2\Xi\tau^{1/2}}{\pi^{1/2}} = \frac{RT\Xi^2}{nF} C_d \quad (225)$$

Hence

$$\tau^{1/2} = \frac{\pi}{4} \frac{C_d}{I_A} a \quad (226)$$

It is thus possible to determine I_0 and α , by varying c_O^* .

4.2.2.3.2. Galvanostatic Double Step. Numerous methods, either analog or digital, have been proposed to cancel out the influence of the double-layer charging current, and have led to modifications either in the experimental device or the treatment of data or both.⁽⁹⁰⁾ The best-known technique is the galvanostatic double step described below.

Gerisher and Krause⁽⁹¹⁾ have devised a way of separating the two following phenomena:

- (i) charging of the double-layer capacity
- (ii) electrochemical reactions.

To this end, they proposed that a pre-impulse of amplitude I_1 be used in order to charge rapidly the double layer, the duration t_1 of this first impulse ranging from 1 to 10 μ s [Table 1(k)].

The ratio I_1/I_2 (where I_2 is the current for $t > t_1$) for a given time t_1 must be chosen so that the double-layer capacity, at the end of charge, is subjected to a potential change ΔE_{t_1} equal to the overpotential η_h , corresponding to the current I_2 :

$$\Delta E_{t_1} = \eta_h \quad (227)$$

Under these conditions, the $\eta = g(t)$ curve exhibits two different parts (Figure 27):

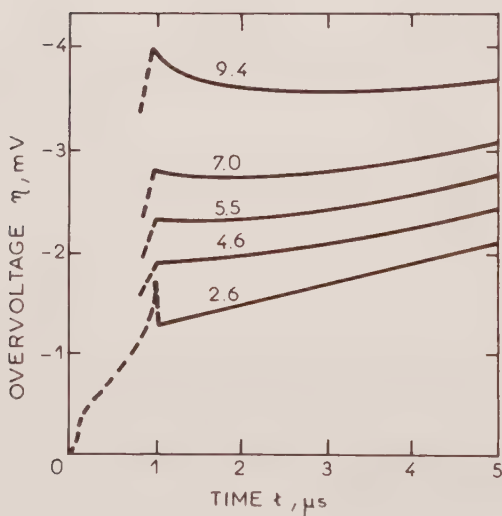


Figure 27. Tracings of η - t curves in the case of galvanostatic double step for the discharge of 5×10^{-4} M mercurous ion on mercury in 0.98 M perchloric acid at 25°C. $I_2 = 19 \text{ mA cm}^{-2}$, $t_1 = 1 \mu\text{s}$. The number on each curve denotes the value of I_1/I_2 . Note the third horizontal tangent. Spurious transient near t_1 and curves for $t < t_1$ represented only for the lower curve [from Reference (93)].

- (i) For $0 \leq t < t_1$ it represents the charging of the capacity
(ii) For $t \geq t_1$ it represents the polarization of the electrode under the influence of I_2 . In that case, if

$$\frac{d\eta}{dt}(t = t_1) = 0 \quad (228)$$

the transfer overpotential corresponding to I_2 is represented by the value of η_h for $t = t_1$.⁽⁹²⁾ If the concentration polarization is disregarded, one has:

$$I_2 = I_0 \frac{nF}{RT} \eta_h \quad (229)$$

or

$$I_2 = \eta_h / R_{ct} \quad (230)$$

Matsuda *et al.*,⁽⁹³⁾ taking account of the concentration polarization, have shown that at low overpotentials:

$$I_F(\eta \rightarrow 0) = I_0 \left(\frac{c_R}{c_R^*} - \frac{c_O}{c_O^*} + \frac{nF}{RT} \eta \right) \quad (231)$$

4.2.2.4. Application to Chronopotentiometry

4.2.2.4.1. *Classical Chronopotentiometry.*⁽⁹⁴⁾ Equation (210) shows that, after a transition time τ , the concentration of the species Ox will be zero at the electrode surface [i.e., $c_O(0, \tau) = 0$]. Hence

$$\tau = \frac{\pi n^2 F^2 A^2 D_O}{4 I_A^2} c_O^{*2} \quad (232)$$

Inserting the values of $c_O(0, t)$ and $c_R(0, t)$ in the Nernst equation [Eq. (43)], one has:

$$E = E^\circ + \frac{RT}{nF} \ln \frac{c_O(0, t)}{c_R(0, t)} \quad (233)$$

That is

$$E = E^\circ + \frac{RT}{nF} \ln \frac{c_O^* - [2I_A/nFA(D_O\pi)^{1/2}]t^{1/2}}{c_R^* + [2I_A/nFA(D_R\pi)^{1/2}]t^{1/2}} \quad (234)$$

If c_O^* is expressed in terms of τ and if $c_R^* = 0$, then

$$E = E_{\tau/4} + \frac{RT}{nF} \ln \frac{\tau^{1/2} - t^{1/2}}{t^{1/2}} \quad (235)$$

with

$$E_{\tau/4} = E_{1/2} = E^\circ + \frac{RT}{2nF} \ln \frac{D_R}{D_O}$$

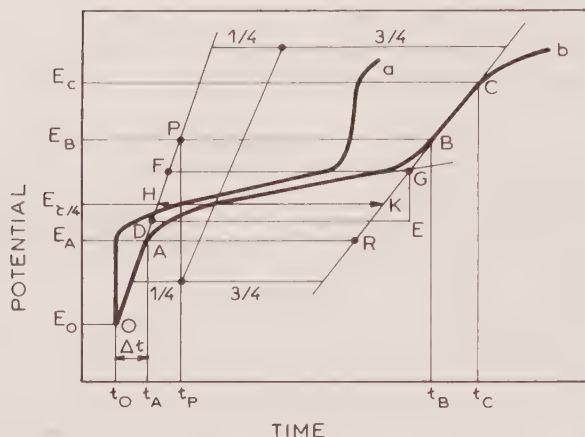


Figure 28. Various experimental definitions of the transition time τ from chronopotentiograms (b), which are distorted by capacity effects [curve (a) is not influenced] [from Reference (90)]. According to Delahay and Mattax, $\tau = HK$, the distance between the extrapolated lines OA and BC at $E_{\tau/4}$. This potential is found at the intersection of the chronopotentiogram with the line connecting the points at 1/4 of the horizontal distance between OA and BC. However, according to Delahay and Mamantov, $\tau = PB$. In a method ascribed to Reinmuth $\tau = DE$ (but Reinmuth used $\tau = FG$).

Even if this transition time τ is theoretically well-defined, there is some problem in measuring it, as shown on Figure 28.

Equation (235) has been extended to electrode processes occurring in several consecutive steps.⁽⁹⁵⁾ Here the bulk concentration c_{Oj}^* of the j th electroactive species is

$$c_{Oj}^* = \frac{2I_A}{n_j F (\pi D_{Oj})^{1/2}} \left[\left(\sum_{m=1}^j \tau_m \right)^{1/2} - \left(\sum_{m=1}^{j-1} \tau_m \right)^{1/2} \right] \quad (236)$$

during the j th step of the chronopotentiogram, which is defined by:

$$\sum_{m=1}^j \tau_m > t > \sum_{m=1}^{j-1} \tau_m$$

Since by Eq. (65)

$$[c_{Oj}^* - c_{Oj}(0, t)] D_{Oj}^{1/2} = c_{Rj}^* D_{Rj}^{1/2} \quad (237)$$

then,

$$[c_{Oj}^* - c_{Oj}(0, t)] D_{Oj}^{1/2} = \frac{2I_A}{n_j F \pi^{1/2}} \left[t^{1/2} - \left(\sum_{m=1}^{j-1} \tau_m \right)^{1/2} \right] \quad (238)$$

where $c_{Oj}(0, t)$ and $c_{Rj}(0, t)$ are the surface concentrations of the oxidized and reduced forms of the j th electroactive species. It is assumed that the initial bulk concentration c_{Rj}^* of the reduced form is zero.

Solving Eqs. (236) and (238) for $c_{Oj}(0, t)$ and substituting into the Nernst equation give the potential-time relationship for the j th step of the chronopotentiogram:

$$E = E_{1/4} + \frac{RT}{n_j F} \ln \frac{\left(\sum_{m=1}^j \tau_m \right)^{1/2} - t^{1/2}}{t^{1/2} - \left(\sum_{m=1}^{j-1} \tau_m \right)^{1/2}} \quad (239)$$

Equation (239) is valid only when the j th couple is reversible. However the reversibility of the electrochemical processes for species $i < j$ is not a necessary condition.

4.2.2.4.2. Derivative Chronopotentiometry. Measuring the transition time τ is often difficult because of the double-layer charge among other reasons. Numerous techniques have been elaborated in order to obtain this characteristic time. For example, the chronopotentiogram can be differentiated electronically (Figure 29) and the quantity dE/dt plotted versus t or E .⁽⁹⁶⁾

For a cathodic (anodic) process, one has $dE/dt < 0$ (>0) respectively. Peters and Burden⁽⁹⁷⁾ have shown that $|dE/dt|$ is related to the transition time. In differentiating Eq. (235) twice and finding the condition for $d^2E/dt^2 = 0$, there results:

$$\left(\frac{dE}{dt} \right)_{\min} = -\frac{27RT}{8nF\tau} \quad (240)$$

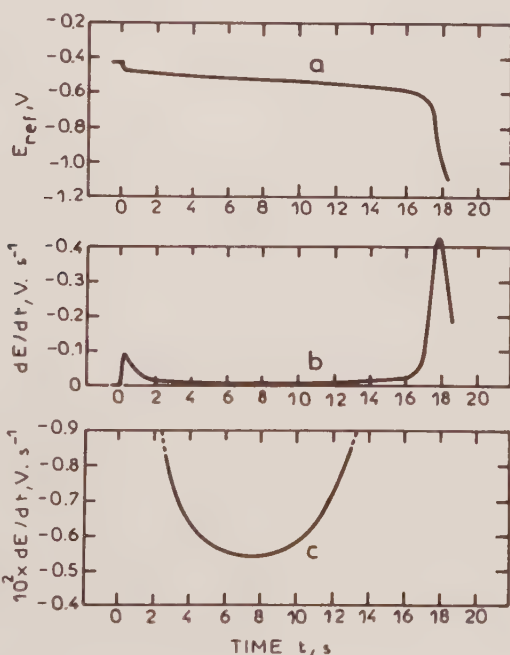


Figure 29. Schematic conventional and derivative chronopotentiograms for thallium(I) reduction, [from Reference (97)]. Curve (a): Conventional chronopotentiogram of $6.28 \cdot 10^{-3} M$ thallium(I) in $0.1 M$ potassium nitrate at mercury pool cathode; $I = 0.503 \text{ mA}$. Curve (b): Derivative chronopotentiogram corresponding to curve (a). Curve c: Derivative chronopotentiogram showing a magnified portion of curve (b) near the region of the minimum.

That is:

$$\left(\frac{dE}{dt}\right)_{\min} = -\frac{0.08664}{n\tau} \quad \text{at } 25^\circ\text{C} \quad (241)$$

According to these authors, $(dE/dt)_{\min}$ is little affected by the double-layer charging currents, and is easier to measure than τ .

This method has been applied to homogeneous chemical reactions and consecutive electrochemical processes.

4.2.2.4.3. Application of the Convolution Procedure to Chronopotentiometry. Nadjo and Saveant⁽⁹⁸⁾ have recently proposed that the convolution procedure be used in chronopotentiometry. It is known that, for a diffusion-controlled electron transfer, one has by Eq. (138), in the case of $D_O^*/D_R^* = 1$:

$$E_{\text{ref}} = E^\circ + \frac{RT}{nF} \ln \frac{\hat{I}_{Fl} - \hat{I}_F}{\hat{I}_F} \quad (242)$$

where

$$E_{\text{ref}} = E + R_e I \quad (243)$$

If the convoluted current $\hat{I}_F(t)$ is calculated for a current step ($I_A = \text{constant}$) by integrating Eq. (136), one has:

$$\hat{I}_F = \frac{2}{\pi^{1/2}} I_A t^{1/2} \quad (244)$$

and

$$\hat{I}_{Fl} = \frac{2}{\pi^{1/2}} I_A \tau^{1/2} \quad (245)$$

Thus one obtains:

$$\tau = \frac{\pi \hat{I}_{Fl}^2}{4 I_A^2} \quad (246)$$

and it is sufficient to plot:

$$\frac{RT}{nF} \ln \frac{\hat{I}_{Fl} - \hat{I}_F}{\hat{I}_F} = \frac{RT}{nF} \ln \frac{\tau^{1/2} - t^{1/2}}{t^{1/2}} \quad (247)$$

versus E_{ref} to obtain E° and τ (Figure 30).

4.2.2.4.4. Chronopotentiometry in the Case of Heterogeneous Reactions. Plotting the potential vs. time curves under galvanostatic or coulometric (charging curve) conditions has been widely used in studying the formation and destruction of adsorbed layers or oxide films at the surface of solid electrodes. The best-known examples of this are the adsorption-desorption of hydrogen and oxygen at noble metals⁽⁹⁹⁾ and the formation of passivating layers on iron, nickel, chromium, and their alloys.⁽¹⁰⁰⁾

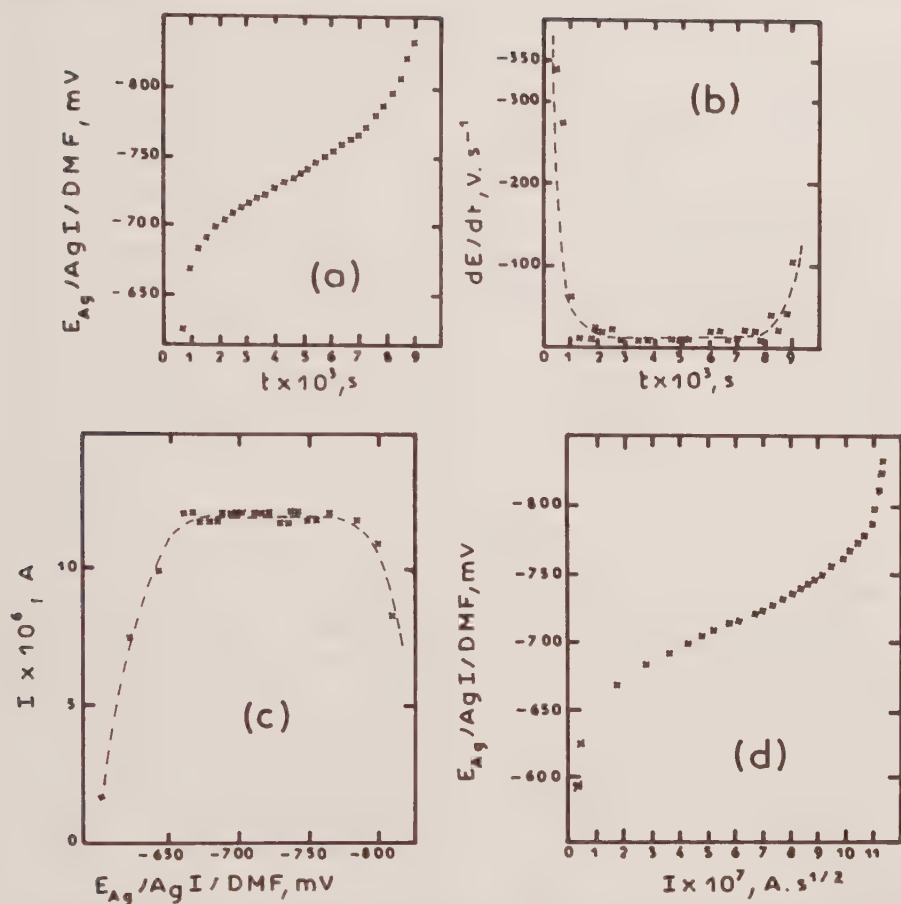


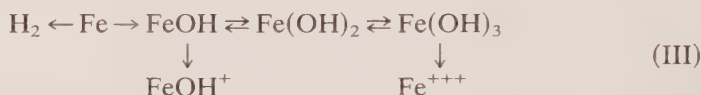
Figure 30. Extraction of the faradaic information. Galvanostatic reduction of 1 mM fluorenone in DMF with 1 M NBu_4BF_4 . Current density: $13 \mu A cm^{-2}$. (a) Initial chronopotentiogram. (b) Differentiation of the electrode potential with respect to time. (c) Faradaic current versus corrected potential. (d) Corrected potential as a function of the convoluted faradaic current [from Reference (98)].

The $E_{ref}(t)$ curves are usually basic in the qualitative analysis of the properties of the layers. It is generally supposed that each potential arrest corresponds to the formation or the destruction of a species.⁽¹⁰¹⁾ Measuring the charge involved during the transition time allows an estimation of the amount of material constituting the layer or the film.

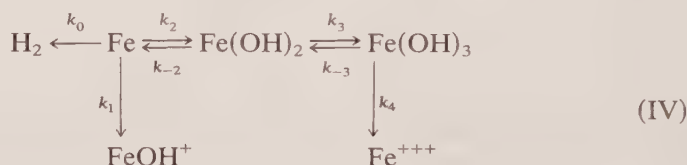
However, there appear major difficulties when one wishes to exploit the curve quantitatively: (i) in general, the value of the potential arrests does not agree with the thermodynamic equilibrium potential of the reactions invoked to explain the formation of the layer; (ii) Determining coulometrically the thickness and the properties of the films requires that all side reactions be

disregarded (oxido-reduction of the medium) and that the reaction mechanism be known rather accurately; (iii) If adsorbed intermediate species are to be considered the equations describing the model cannot be integrated analytically and it is necessary to use a computer. These problems become more obvious in the case of passivating layers. As an example, we shall give below a quantitative treatment of the chronopotentiogram for iron reactivation in terms of a dissolution-passivation reaction mechanism (Flade's experiment).

This experiment is based on interrupting the current polarizing an iron electrode within the passivity range in acidic medium. Depassivation is studied by recording the evolution of the potential (open-circuit potential decay). The transition time is defined here by the time needed to reach the so-called Flade potential. This potential decay has been simulated using a computer by considering the following dissolution-passivation mechanism for iron in molar sulfuric acid aqueous solution:



Since the processes of interest take place at relatively high anodic potentials, FeOH forms rapidly and does not determine the rate of the overall process. The mechanism has been simplified to:



Assuming that θ_1 and θ_2 are the fractional coverages of Fe(OH)_2 and Fe(OH)_3 , the interface behavior can be described by:

$$\beta_1 \frac{d\theta_1}{dt} = (1 - \theta_1 - \theta_2)k_2 - \theta_1 k_{-2} - \theta_1 k_3 + \theta_2 k_{-3} \quad (248)$$

$$\beta_2 \frac{d\theta_2}{dt} = \theta_1 k_3 - \theta_2 k_{-3} - \theta_2 k_4 \quad (249)$$

$$I_F/FA = 2(1 - \theta_1 - \theta_2)(k_2 - k_0 + k_1) - \theta_1(k_{-2} - k_3) - \theta_2 k_{-3} \quad (250)$$

Taking account of the double-layer capacity, Eq. (248) to (250) can be integrated using a predictor-corrector method. One thereby obtains the simulated curves a and b in Figure 31 which express the evolution of the potential and fractional coverages. The simulated potential decay is in excellent agreement with the experimental results.⁽¹⁰²⁾

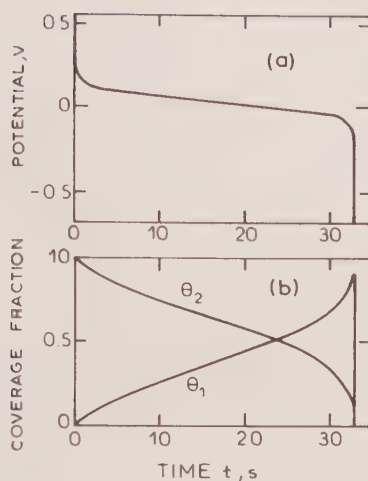


Figure 31. Computer simulation of the Flade experiment [from Reference (102)] (a) Potential decay curve. (b) Time variation of the fractional coverages of the surface: θ_1 for Fe(OH)_2 and θ_2 for Fe(OH)_3 .

4.2.2.5. Measurement of the Ohmic Drop—Interrupter Method

The resistance of the electrolyte existing between the equipotential surface defined by the reference electrode and the working electrode leads to a potential drop, called ohmic drop, between the two electrodes. To obtain an approximate value of the interface potential, it is often necessary to measure the ohmic drop and to subtract it from the potential actually measured between the working electrode and the reference electrode. As a matter of fact, even if the geometry of the cell is chosen so that the ohmic drop is diminished, using, for example, a Luggin capillary, or if electronic compensation is used, there still remains a part of it that has to be measured.

The most frequently used method to measure ohmic drop, apart from impedance measurements at high frequencies, consists of interrupting the polarization current (called the interrupter method). The potential response, observed with a wide-band oscilloscope, presents a steep jump ΔE (Figure 32a) due to the ohmic drop. This jump is followed by an exponential-like decay caused by the double-layer capacity and the faradaic processes. It is assumed that ΔE is equal to the overall ohmic drop between the reference electrode and the working electrode. By measuring the direct polarization current I just before interrupting, the electrolyte resistance can be calculated as:

$$R_e = \Delta E / I \quad (251)$$

In fact, according to Newman *et al.*,⁽¹⁰³⁾ this resistance would be characteristic of the primary current distribution only, i.e., the distribution existing in the presence of infinitely fast faradaic and mass transfer processes (absence of electrochemical overpotentials). The ohmic drop characteristic of the secondary distribution (taking account of the faradaic processes) varies from one

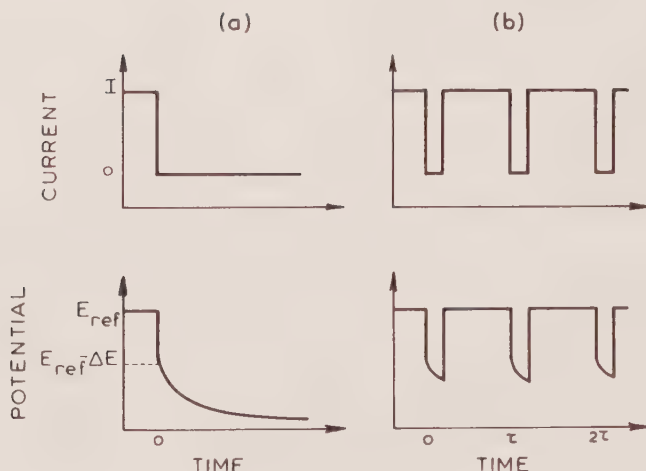


Figure 32. Interrupter method for measuring the electrolyte resistance ($R_e = \Delta E/I$). (a) Single measurement: potential response to current interruption. (b) Repetitive measurement allowing observation by means of an oscilloscope.

point to another at the interface and, strictly speaking, would not be accessible to direct measurement.

The interruption of the polarization current can be performed in two ways:

- (i) using a relay with a very short cut-off time (of the order of some 10^{-9} s), for example, a mercury wetted contact relay.
- (ii) using a fast diode, which is polarized in reverse by an electric impulse.

It can be noted that, in both these methods, by keeping the circuit open during a very short time (about $100 \mu\text{s}$) and at a recurrence frequency of some tens of hertz, the repetitive signal can be observed more readily with a wide-band oscilloscope without perturbing, in a significant way, the phenomenon under investigation (Figure 32b).

4.2.3. Charge Step Method^(104,105)

In this method, the electrode (initially at its equilibrium potential E_{eq}) is perturbed from equilibrium by the passage of a given charge during a very short time (0.1 to $10 \mu\text{s}$) and the potential shifts from E_{eq} to $E(0) = E_{eq} + \eta(0)$. The relaxation of the electrode back to equilibrium is followed by the measurement of the electrode overvoltage $\eta(t)$ vs. time. At time zero, the charge density of the electrode is changed abruptly, so that the leakage current due to the charge transfer resistance can be neglected during charging. The experiment is performed by discharging a capacitor in the electrochemical cell in such a way that the cell is essentially at open circuit (zero current) once

charging is completed. The charge increment $\Delta Q = Q(0) - Q_i$ (where Q_i and $Q(0)$ are the initial and total charges, the end of charging being $t = 0$) is consumed progressively by the electrode reactions, so that the potential drifts back to its initial equilibrium value [Table 1(1e)]. The overvoltage-time variation depends on the charge increment, the double-layer capacity, and the processes taking place at the electrode.

The overvoltage $\eta(t) = E(t) - E_{eq}$ is after the end of charging:

$$\eta(t) = \frac{Q(t) - Q_i}{C_d} \quad (252)$$

if C_d is assumed to be constant within the potential range explored. Since the double-layer capacity discharges through the faradaic current, one has:

$$Q(t) = Q(0) + \int_0^t I_F(t) dt \quad (253)$$

Hence

$$\eta(t) = \frac{Q(0) - Q_i}{C_d} + \frac{1}{C_d} \int_0^t I_F(t) dt \quad (254)$$

$$\eta(t) = \eta(0) + \frac{1}{C_d} \int_0^t I_F(t) dt \quad (255)$$

Calculation of the actual n - t curve requires the knowledge of the explicit form of the current-potential relationship. We shall consider two cases, a pure charge transfer and a charge transfer controlled by diffusion. Calculation has been performed only when the perturbation from equilibrium is small, i.e., $|\eta| < 5$ mV.

4.2.3.1. Pure Charge Transfer

In this case, one has:

$$I_F = I_0(nF/RT)\eta \quad (256)$$

Hence by Eq. (255), one obtains

$$\eta(t) = \eta(0) \exp \left[-\frac{I_0}{C_d} \left(\frac{nF}{RT} \right) t \right] \quad (257)$$

Thus the $\log \eta$ vs. t curve is a straight line and I_0 can be computed from its slope. The transfer coefficient α is obtained by varying the concentration of the reactant and C_d is determined from independent measurements or by:

$$\eta(0) = \Delta Q / C_d \quad (258)$$

4.2.3.2. Charge Transfer Controlled by Diffusion

In this case, one has by Eqs. (212) and (254):

$$I_F(t) = nF \frac{\partial c_0}{\partial z}(0, t) = I_0 \left[\frac{c_0}{c_0^*} - \frac{c_R}{c_R^*} - \frac{nF}{RT} \frac{\Delta Q}{C_d} - \frac{(nF)^2 D_O}{RTC_d} \int_0^t \frac{\partial c_0}{\partial z}(0, t) dt \right] \quad (259)$$

Using the Laplace transform, Delahay⁽¹⁰⁴⁾ showed that:

$$I_F(t) = -I_0 \frac{nF}{RT} \frac{\Delta Q}{C_d} \frac{1}{a-b} \{ a[\exp(a^2 t)] \operatorname{erfc}(at^{1/2}) - b[\exp(b^2 t)] \operatorname{erfc}(bt^{1/2}) \} \quad (260)$$

The coefficients a and b depend on c_0^* , c_R^* , D_O , D_R , and C_d . The overvoltage is derived by integrating Eq. (255):

$$\eta(t) = \eta(0) - I_0 \frac{nF}{RT} \frac{\Delta Q}{C_d} \frac{1}{a-b} \left\{ \frac{1}{b} [1 - (\exp(b^2 t)) \operatorname{erfc}(bt^{1/2})] - \frac{1}{a} [1 - (\exp(a^2 t)) \operatorname{erfc}(at^{1/2})] \right\} \quad (261)$$

Delahay has shown that for

$$4 \frac{nF}{RT} \frac{1}{C_d I_0} \gg \left[\frac{1}{nF} \left(\frac{1}{c_O^* D_O^{1/2}} + \frac{1}{c_R^* D_R^{1/2}} \right)^2 \right] \quad (262)$$

the processes taking place at the interface are purely controlled by charge transfer and therefore Eq. (257) holds again.

In addition, if

$$4 \frac{nF}{RT} \frac{1}{C_d I_0} \ll \left[\frac{1}{nF} \left(\frac{1}{c_O^* D_O^{1/2}} + \frac{1}{c_R^* D_R^{1/2}} \right)^2 \right] \quad (263)$$

the processes are purely diffusion-controlled.

In Figure 33, some experimental results are presented where pure control by charge transfer is observed.

Note that Reinmuth⁽¹⁰⁵⁾ described more complex calculations by taking account of complications arising from chemical reactions.

4.2.4. Step Response Analysis in the Complex Plane

Considering the complexity of the current-time relationships in the case of potential or current step perturbation, some authors proposed the analysis of the responses in the complex plane.⁽¹⁰⁶⁻¹⁰⁸⁾ To this end the response is studied using the Laplace transform. By Eq. (44), using the real axis only,

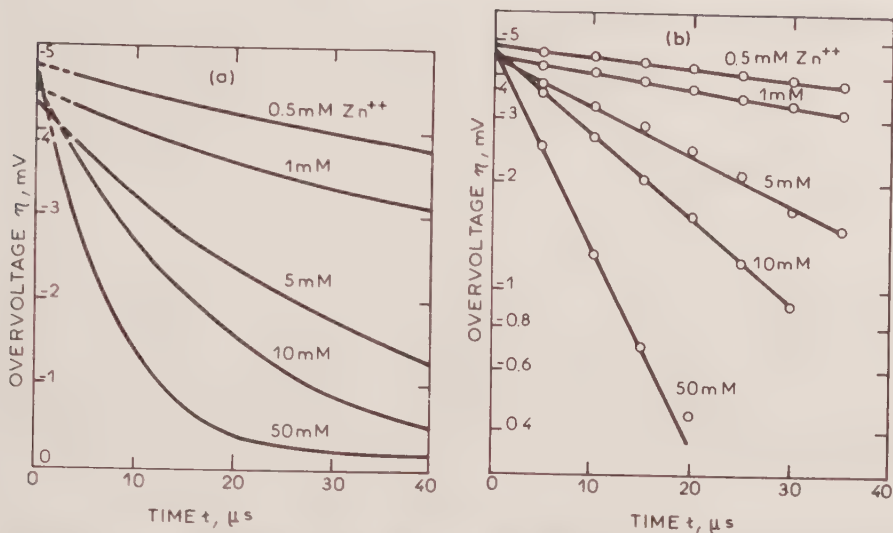


Figure 33. Charge step method [from Reference (104)]. Curve (a): Overvoltage–time curves for Zn^{+2} discharge on Zn-amalgam at different Zn^{2+} concentrations in 1 M KCl; dashed parts are extrapolated to the overvoltage obtained from curve (b) at time zero. Curve (b): Time dependence of the logarithm of the overvoltage under the same conditions as for curve (a).

there results:

$$F(\sigma) = \int_0^{\infty} f(t) e^{-\sigma t} dt \quad (264)$$

Although a generalization of this procedure to non-linear cases⁽¹⁰⁹⁾ has been proposed, it is really advantageous only when small perturbations are employed. By performing a transform on the response and on the perturbation, we can derive the concept of operational impedance, i.e.,

$$Z(\sigma) = \frac{V(\sigma)}{I(\sigma)} \quad (265)$$

In the case of a diffusion-controlled electron transfer, we have for small perturbations, by Eq. (212):

$$\mathcal{L}I_F(s) = I_0 \left[\frac{\mathcal{L}c_O(0, s)}{c_O^*} - \frac{\mathcal{L}c_R(0, s)}{c_R^*} - \frac{nF}{RT} \mathcal{L}E(s) \right] \quad (266)$$

Solving Fick's equation gives:

$$\begin{aligned} \frac{\mathcal{L}c_O(0, s)}{c_O^*} &= -\frac{\mathcal{L}I_F(s)}{nFAc_O^*D_O^{1/2}s^{1/2}} + \frac{1}{s} \\ \frac{\mathcal{L}c_R(0, s)}{c_R^*} &= \frac{\mathcal{L}I_F(s)}{nFAc_R^*D_R^{1/2}s^{1/2}} + \frac{1}{s} \end{aligned} \quad (267)$$

and hence

$$\mathcal{L}E(s) = -\frac{RT}{nF} \mathcal{L}I_F(s) \left[\frac{1}{I_0} + \frac{1}{nFA s^{1/2}} \left(\frac{1}{c_O^* D_O^{1/2}} + \frac{1}{c_R^* D_R^{1/2}} \right) \right] \quad (268)$$

Consequently:

$$Z(s) = -R_{ct} \left(1 + \frac{I_0 \Xi}{s^{1/2}} \right) \quad (269)$$

It must be noted that if $s = j\omega$ the expression of the impedance [Eq. (79)] is found again, since Eq. (165) holds, as could be expected by the fact that this technique is equivalent to impedance methods.

From an experimental standpoint, one has to sample the response analyzed, and then apply an algorithm which allows one to calculate $Z(s)$. Pilla recommends that the following expression be used:⁽¹⁰⁸⁾

$$F(\sigma) = \sum_i \left\{ \frac{[f(t_{i+1}) e^{-\sigma t_{i+1}} - f(t_i) e^{-\sigma t_i}][t_{i+1} - t_i]}{\ln [f(t_{i+1}) e^{\sigma t_{i+1}} / f(t_i) e^{\sigma t_i}]} \right\} + \frac{f(t_x)}{\sigma} \quad (270)$$

As an example, we give the impedance of an electrode at which a diffusion-controlled transfer takes place (Figure 34). The theoretical expression of the impedance is in that case

$$Z(s) = R \frac{\tanh (s \delta_N^2 / D)^{1/2}}{(s \delta_N^2 / D)^{1/2}} + R_{ct} \quad (271)$$

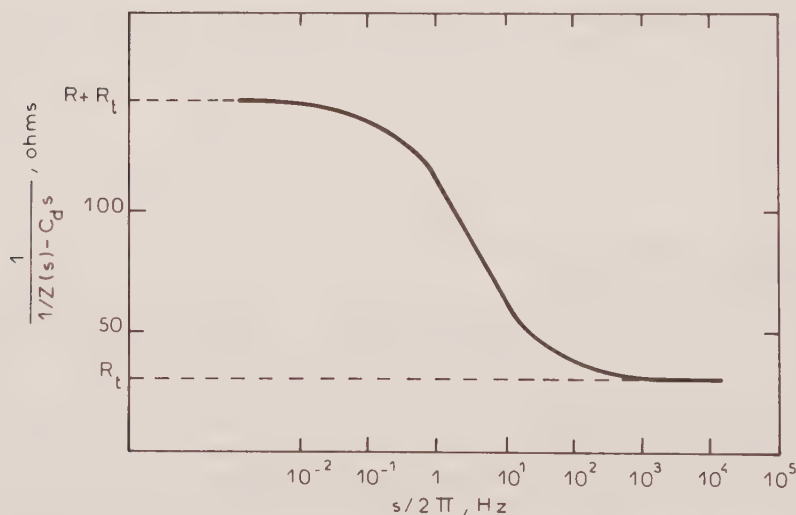


Figure 34. Variation of the impedance vs. the Laplace variable s after elimination of the double-layer capacity C_d , in the case of a diffusion-controlled transfer [from Reference (110)].

if a motionless diffusion-layer of thickness δ_N (Nernst's layer) is considered (where $R = R_{ct}k\delta_N/D$).

4.3. Exponential Techniques

Rangarajan^(111,112) has proposed that an exponential-shaped current perturbation of the form (Figure 35a):

$$I(t) = \Delta I \exp(-t/\tau) \quad (272)$$

be used to analyze the behavior of the electrochemical interface.

With this technique certain types of processes can be analyzed in a simple way. For example, in analyzing Tafel's law in corrosion studies, it is necessary to determine α and I_0 which are related to the current I by Eq. (1). Hence

$$\eta = \frac{RT}{\alpha nF} \ln \frac{I}{I_0} \quad (273)$$

The potential response to the exponential-shaped current perturbation given by Eq. (272) leads to:

$$\eta(t) = \frac{RT}{\alpha nF} \left(-\frac{t}{\tau} \right) + \frac{RT}{\alpha nF} \ln \frac{\Delta I}{I_0} \quad (274)$$

In plotting $\eta(t)$ as a function of t/τ , one obtains a straight line whose slope, $RT/\alpha nF$, and intercept with the time axis, $(RT/\alpha nF) \ln(\Delta I/I_0)$ give α and I_0 , respectively.

Similarly, in the case of a diffusion-controlled electron transfer, perturbed by an exponential signal, one has by Eqs. (63) and (64):

$$c_i(0, t) = c_i^* + \varepsilon \frac{\Delta I}{nFA(\pi D_i/\tau)^{1/2}} \int_0^{t/\tau} \frac{e^{-Z} dZ}{(t/\tau - Z)^{1/2}} \quad (275)$$

with $\varepsilon = +1$ if i denotes the reduced species and $\varepsilon = -1$ if i denotes the oxidized species. Hence

$$\frac{\Delta c_i}{c_i^*} = \varepsilon \frac{\Delta I}{nFAc_i^*(\pi D_i/\tau)^{1/2}} \mathcal{D}[(t/\tau)^{1/2}] \quad (276)$$

where

$$\mathcal{D}(u) = e^{-u^2} \int_0^u \exp x^2 dx \quad (277)$$

is the Dawson's integral, a tabulated function whose shape is given in Figure 35a.

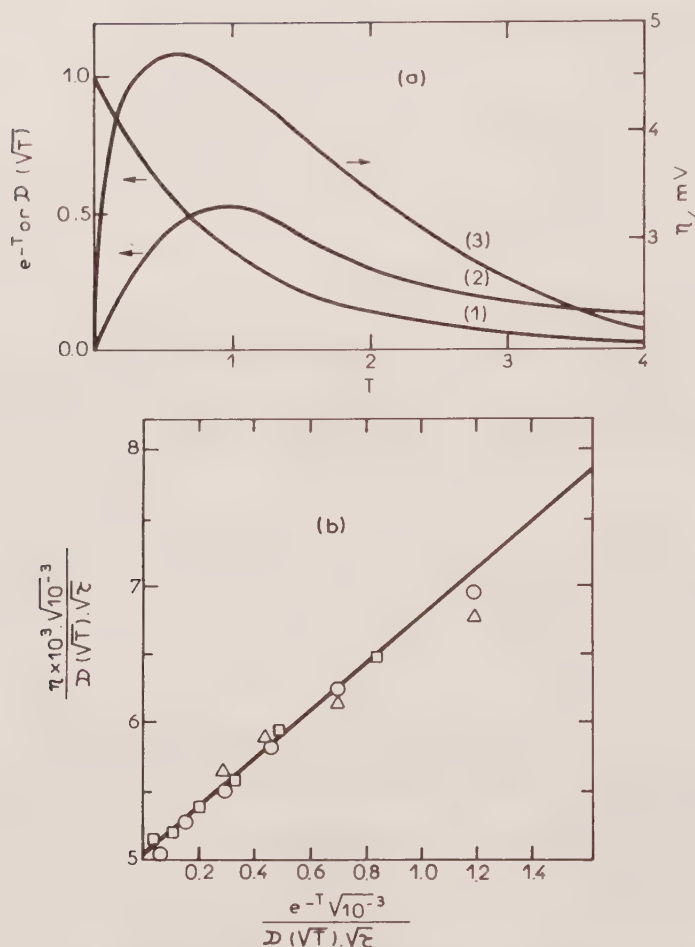


Figure 35. Exponential relaxation technique [from Reference (111)]. Curve (a): Variation of (1) e^{-T} , (2) $\mathcal{D}(T^{1/2})$ and (3) $\eta(t)$ vs. $T = t/\tau$. Curve (b): Multi-curve plot of the $\eta(t)/\mathcal{D}(T^{1/2})\tau^{1/2}$ vs. $\exp(-T)/\mathcal{D}(T^{1/2})\tau^{1/2}$ for ferrocyanide-ferricyanide at different values of RC : (O) 1 ms, ($\square$) 2 ms, ($\triangle$) 10 ms.

In the case of a small-amplitude perturbation, it can be established from Eq. (212) that:

$$I_F(t) = I_0 \left(\frac{\Delta c_O}{c_O^*} - \frac{\Delta c_R}{c_R^*} - \frac{nF}{RT} \eta \right) \quad (278)$$

Therefore:

$$\eta(t) = \Delta t \cdot R_{ct} \{ \exp(-t/\tau) + \gamma \mathcal{D}[(t/\tau)^{1/2}] \} \quad (279)$$

where R_{ct} is the charge transfer resistance and:

$$\gamma = \frac{2I_0}{nFAc_O^*(\pi D_O/\tau)^{1/2}} \left[1 + \frac{c_O^*}{c_R^*} \left(\frac{D_O}{D_R} \right)^{1/2} \right] \quad (280)$$

In plotting $\phi(T) = \eta(t)/\mathcal{D}[(t/\tau)^{1/2}]\tau^{1/2}$ as a function of $U(t) = \exp(-t/\tau)/\mathcal{D}[(t/\tau)^{1/2}]\tau^{1/2}$, a straight line is obtained which is independent of τ , and whose slope and intercept with the time axis are $\Delta I \cdot R_{ct}$ and $\Delta I \cdot R_{ct}\gamma/\tau^{1/2}$, respectively. Plotting this line for different τ -values allows one to diminish considerably the errors in the measurements as depicted in Figure 35b.

Rangarajan has also proposed a method aiming to correct the double-layer charging as well as an application of this technique to chemical reactions preceding the electron charge transfer.

5. Other Relaxation Techniques⁽⁴⁾

We have already seen that a certain number of quantities other than the electric ones such as A , P , T , c_i^* , and Ω can be used to perturb the state of the electrode. Some of these methods (namely those involving A , P , T) are inspired by techniques used to study homogeneous chemical kinetics, in which electric quantities cannot be employed and therefore other types of quantities have to be perturbed. In electrochemistry, such methods can be used in the case of poorly conducting electrolytes, for example, for which the use of electric quantities gives rise to certain problems. In general, the equilibrium state is perturbed and the relaxation of the potential is observed at open circuit.

5.1. Area Perturbation Techniques

It can be easily understood that if the area A of an electrode varies, the double-layer capacity varies accordingly and a charging current appears. In open circuit, this current has to be compensated by a faradaic current, thus leading to an overpotential η .⁽¹¹³⁾

As an example, the current-potential characteristics of a redox system can be determined in open circuit (i.e., polarized at the rest potential). The capacitive current is obtained by varying the electrode charge

$$Q = C_d(E - E_z)A \quad (281)$$

where C_d is the double-layer capacity and E_z the potential of zero charge. The charging current is then:

$$I_C = \frac{dQ}{dt} = (E - E_z)A \frac{dC_d}{dE} \cdot \frac{dE}{dt} + C_d A \frac{dE}{dt} + C_d (E - E_z) \frac{dA}{dt} \quad (282)$$

In open circuit, as $I_C + I_F = 0$, we have:

$$(E - E_z)A \frac{dC_d}{dE} \cdot \frac{dE}{dt} + C_d A \frac{dE}{dt} + C_d (E - E_z) \frac{dA}{dt} + I_F = 0 \quad (283)$$

This method can be used with liquid metals only, and cannot be easily applied to solid electrodes. Experimentally, one utilizes the streaming mercury electrode in which a continuous flow of mercury is oriented towards the surface of the solution at a given angle (of 45° in general). In this case

$$I_C = C_d(E - E_z) \frac{2m}{rd} \quad (284)$$

where d is the density of mercury, m the rate of flow of mercury, and r the radius of the capillary.

When no electrode reaction occurs, then $I_F = I_C = 0$, and this technique constitutes a method for determining the potential of zero charge.

In the case of a diffusion-controlled charge transfer, it can be shown that for small η

$$-\frac{1}{\eta} = 2 \frac{nF}{RT} \cdot \frac{1}{A\Xi} \cdot \frac{rd^{1/2}}{C_d(E - E_z)} \cdot \left(\frac{l}{m}\right)^{1/2} \left[1 - \frac{1}{M} \ln(1 + M) \right] \quad (285)$$

with

$$M = \pi rd^{1/2} A\Xi \left(\frac{l}{m}\right)^{1/2} \cdot I_0 \quad (286)$$

and l = the length of the mercury column.

If $M \rightarrow \infty$, then the process is purely diffusion-controlled and if $M \rightarrow 0$, purely charge transfer-controlled.

Use of a vibrating electrode, leading to a sinusoidal distortion of the meniscus, constitutes another area perturbation technique.⁽¹¹⁴⁾ Renewing of the surface of solid electrodes can also be considered as a technique of this type. The surface of the metal is renewed by continuous scouring with a rapidly rotating corundum disk, and the polarization curves are recorded during this operation. Another method consists of removing an oxide by abrasion and in observing the transient repassivation signal.^(115,116)

5.2. Pressure Perturbation Techniques

A reversible electrode can be removed from equilibrium by a pressure perturbation. In that case, the relaxation of the open-circuit potential is analyzed. For example, pressure jumps of about 100 atm can be produced in some tens of μ s using the bursting of a metal diaphragm.

Dumargue⁽¹¹⁷⁾ has used a sinusoidal perturbation of pressure with a small amplitude ΔP .

$$\Delta P(t) = \Delta P \sin 2\pi\nu t \quad (287)$$

within a frequency range: $20 \text{ Hz} \leq \nu \leq 2000 \text{ Hz}$. This perturbation induces a variation of the electric charge density at the electrode surface, and hence a

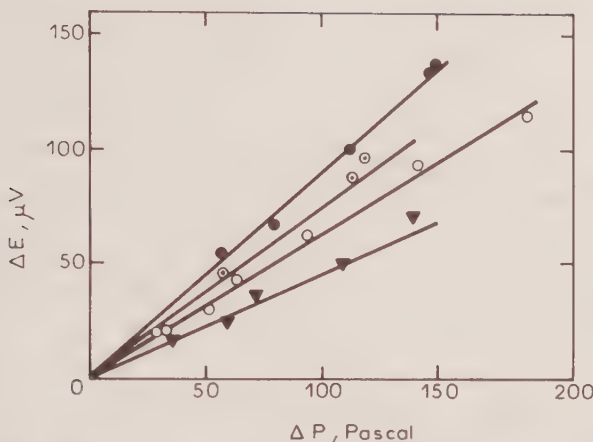


Figure 36. Pressure perturbation technique [from Reference (117)]. Magnitude of the perturbation of potential ΔE induced by a pressure perturbation ΔP for various modulation frequencies: ● 500 Hz, ○ 600 Hz, ○ 700 Hz, ▼ 800 Hz.

potential change of the form

$$\Delta E(t) = \Delta E \cos 2\pi\nu t \quad (288)$$

which represents the response of the double layer to the perturbation. ΔE and all the parameters of interest can be determined. For ΔP of about 100 Pascal (10^{-3} atm), ΔE values of some tens of μV have been found (Figure 36).

5.3. Temperature Perturbation Techniques

This type of perturbation seems *a priori* to be very attractive but exhibits several difficulties from a technological standpoint. As a matter of fact, a temperature change occurring uniformly is difficult to obtain. The temperature can be raised rapidly by using an electric pulse applied to a heater and the subsequent change in electrode potential analyzed. Harima and Aoyagui⁽¹¹⁸⁾ give the following expression for the potential vs. time curve for pure charge transfer assuming a linear change of the temperature at the electrode surface:

$$E(t) = E^\circ(t) - a\tau \left[\frac{dE^\circ}{dT} + \left(\frac{\partial \sigma^M}{\partial T} \right)_{P,E} \cdot \frac{1}{C_d} \right] [1 - \exp(-t/\tau)] \quad (289)$$

when $E^\circ(t)$ is the standard potential, a the rate of increase in temperature at the electrode surface, σ^M the surface charge density of the electrode metal, and τ the characteristic time of the potential change defined by:

$$\tau = C_d RT / n^2 F^2 k_s c^* \quad (290)$$

k_s is the standard rate constant, c^* the common concentration of the reactants, and T the average temperature during the observation. Equation (289) is illustrated in Figure 37 for various τ values.

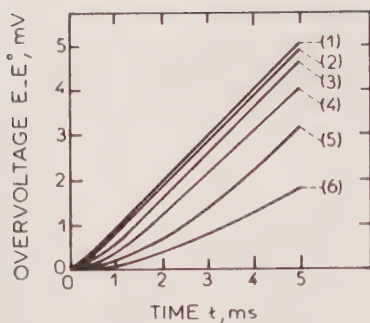


Figure 37. Temperature perturbation technique [from Reference (118)]. Theoretical relaxation curves for a linear change of the temperature at the electrode surface, calculated from Eq. (290) in which $a(dE^\circ/dT) = 1 \text{ V s}^{-1}$ and $(\partial\sigma^M/\partial T)_{P,E} = 0$, and for different values of τ : curve (1) $\tau = 0$, (2) 0.2 ms, (3) 0.5 ms, (4) 1 ms, (5) 2 ms, (6) 5 ms.

Barker and Gardner⁽¹¹⁹⁾ have proposed to illuminate the electrode surface with a long wavelength light which causes a heating of the electrode due to the fact that a part of this light energy is absorbed by the surface. Thus, using a laser the electrode surface is illuminated by a light beam modulated at $f_m = 100 \text{ MHz}$ during short times ($1 \mu\text{s}$). According to Barker, the temperature change would be $0.2^\circ\text{C} \cdot \mu\text{s}^{-1}$ for a light flux of $2 \text{ Joule} \cdot \text{s}^{-1}$.

Ishikawa and Okamoto⁽¹²⁰⁾ have studied the passivity of stainless steels by imposing a temperature perturbation, and have recorded the passivity current as a function of a stepwise temperature increase (see Figure 38).

5.4. Concentration Perturbation Techniques⁽⁴⁾

It is possible to impose a concentration perturbation by placing the electrode in a cell in which the solution is removed at high speed, and then changing rapidly the concentration. The potential relaxation is then observed at open circuit. This classical continuous-flow technique as well as the stop-flow technique can be applied to determine charge transfer rate constants.

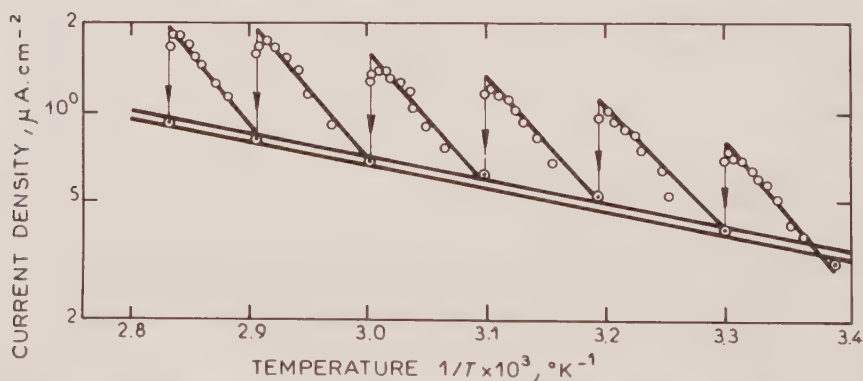


Figure 38. Temperature perturbation technique [from Reference (120)]. Arrhenius curves for the steady state anodic current of passive stainless steel at $+0.4 \text{ V/SCE}$ in $5\% \text{ H}_2\text{SO}_4$ obtained by means of stepwise temperature rise (using an interval of 10°C for each step).

Oldham and Spanier⁽⁵⁷⁾ have proposed to control the concentration of the species at the interface by imposing a current obeying a given law. As a matter of fact, transforming Eq. (61) in the same way as was done with Eq. (63), one can write in the case of species *Ox*:

$$\frac{I_F(t)}{nFA} = c_O^* \left(\frac{D_O}{\pi t} \right)^{1/2} - \left(\frac{D_O}{\pi} \right)^{1/2} \int_0^t \frac{c_O(0, \theta) d\theta}{(t - \theta)^{1/2}} \quad (291)$$

If a constant concentration is to be obtained at the electrode surface, i.e., $c_O(0, t) = \bar{c}_O$ at $t > 0$, then by Eq. (292) it is necessary that the current imposed be such that:

$$I_F(t) = nFA(c_O^* - \bar{c}_O) \left(\frac{D_O}{\pi} \right)^{1/2} \cdot \frac{1}{t^{1/2}} \quad (292)$$

If a concentration ramp is to be obtained, i.e.,

$$c_O(0, t) = c_O^* - \dot{c}t \quad \text{at } t > 0 \quad (293)$$

then it is necessary that the current imposed be such that:

$$I_F(t) = 2nFA\dot{c} \left(\frac{D_O}{\pi} \right)^{1/2} t^{1/2} \quad (294)$$

5.5. Rotation Speed Perturbation Techniques

The advantage of the rotating disk electrode is that mass transport can be controlled by the rotation speed Ω . Thus, perturbing the rotation speed amounts to perturbing mass transport. Based on this idea, some authors⁽¹⁰⁵⁻¹⁰⁷⁾ have suggested imposing either a sweep, or a jump, or a sinusoidal modulation of the rotation speed of the disk electrode, and then analyzing the current response. In this study the equation of convective diffusion is

$$\frac{\partial c}{\partial t} = D\nabla^2 c - \mathbf{v} \cdot \nabla c \quad (295)$$

c being the concentration of species (either *Ox* or *Red*).

5.5.1. Rotation Speed Sweep⁽¹²¹⁾

A rotation speed change of the type $\Omega^{1/2} = at$ seems quite attractive since the Levich equation gives the limiting diffusion current I_l :

$$I_l = 0.62nFA\Omega^{1/2}D^{2/3}\nu^{-1/6}[c_O^* - c_O(0, t)] \quad (296)$$

Therefore, plotting I_l as a function of $\Omega^{1/2}$ allows one to measure the characteristic parameters of the process investigated.

5.5.2. Rotation Speed Step⁽¹²¹⁾

When the electrode surface is suspected to vary under the influence of poisoning or degradation, it may be advantageous to impose a rotation speed step (Figure 39a).

For a diffusion-controlled electron transfer, the equation for the variation of the concentration of the diffusing species can be obtained from Eq. (295):

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} - v(z, t) \frac{\partial c}{\partial z} \quad (297)$$

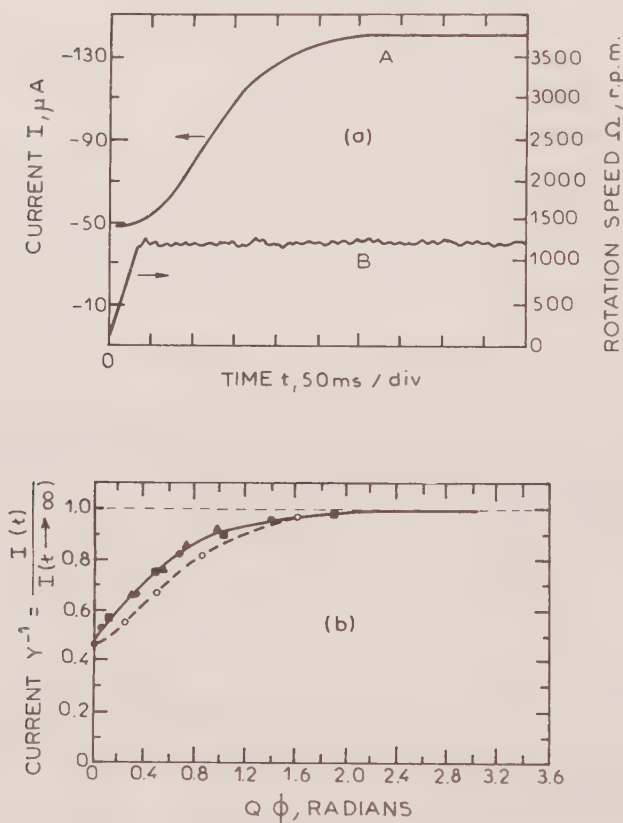


Figure 39. Rotation speed step technique. Curve (a): Oscilloscope traces of a rotation speed step experiment. Trace A: disk current, microamperes. Trace B: disk speed (revolutions per minute). Horizontal sensitivity 50 ms/div for programmed speed step from 144 to 1211 rpm. Disk potential 0.0 V/SCE. Solution: 2.17 mM Fe^{3+} in 1 M H_2SO_4 ; Pt disk. Curve (b): Comparison of normalized theoretical and experimental rotation speed step for Fe^{3+} , Hg_2^{2+} and Ag^+ reductions. Solid curves are computer calculated from Eq. (305). Experimental points are plotted as Y^{-1} vs. $Q \cdot \phi$ for normalization [from Reference (121)].

Hence

$$\int_0^{\infty} \frac{\partial c}{\partial t} dz = -D \frac{\partial c}{\partial z}(0, t) - \int_0^{\infty} v(z, t) \frac{\partial c}{\partial z} dz \quad (298)$$

If c is assumed to vary within a diffusion layer of thickness δ_N (Nernst layer), then integration must be performed up to δ_N instead of to infinity.

In addition, we have

$$c(z, t) = \begin{cases} c(0, t) + [c^* - c(0, t)] \frac{z}{\delta_N} & \text{for } 0 \leq z < \delta_N \\ c^* & \text{for } z \geq \delta_N \end{cases} \quad (299)$$

Hence

$$\frac{\partial c}{\partial t}(z, t) = -\frac{c^* - c(0, t)}{\delta_N^2} z \frac{\partial \delta_N}{\partial t}$$

and

$$\begin{aligned} \frac{\partial c}{\partial z}(z, t) &= \frac{c^* - c(0, t)}{\delta_N} & \text{for } 0 \leq z \leq \delta_N \\ \frac{\partial c}{\partial z} &= \frac{\partial c}{\partial z} = 0 & \text{for } z \geq \delta_N \end{aligned} \quad (300)$$

In this derivation the $\partial c / \partial t(0, t)$ term has been neglected. This is only valid when the redox reaction is very fast or in the case of pure diffusion control [$c(0, t) = 0$].

In integrating, we have:

$$-\int_0^{\delta_N} \frac{c^* - c(0, t)}{\delta_N^2} z \frac{\partial \delta_N}{\partial t} dz = -D \frac{c^* - c(0, t)}{\delta_N} - \int_0^{\delta_N} v(z, t) \frac{c^* - c(0, t)}{\delta_N} dz \quad (301)$$

Hence

$$\frac{1}{2} \frac{\partial \delta_N}{\partial t} = \frac{D}{\delta_N} + \int_0^{\delta_N} \frac{v(z, t)}{\delta_N} dz \quad (302)$$

Since a rotation speed step is applied at time $t = 0$ ($\Omega_1 \rightarrow \Omega_2$), one has

$$\begin{aligned} v(z, t) = v_1(z) &= -0.51 \left(\frac{\Omega_1^3}{\nu} \right)^{1/2} z^2 & \text{at } t < 0 \\ v(z, t) = v_2(z) &= -0.51 \left(\frac{\Omega_2^3}{\nu} \right)^{1/2} z^2 & \text{at } t > 0 \end{aligned} \quad (303)$$

Since $\delta_N(t) \rightarrow \delta_{Nl}$ at $t \rightarrow \infty$ integration of Eq. (302) leads to

$$\phi = \frac{A}{Q} \int_L^Y \frac{\theta d\theta}{(1 - \theta^3)} \quad (304)$$

with $A = 1.3125$; $Q = 0.8058 (D/\nu)^{1/3}$; $Y = \delta_N/\delta_{NI} = I(t \rightarrow \infty)/I(t)$; $\delta_{NI} = 1.6116 (D/\nu)^{1/3} (\nu/\Omega_2)^{1/2}$; and $L = I(t \rightarrow \infty)/I(t = 0)$

Hence

$$\phi = F(Y) - F(L) \quad (305)$$

where

$$F(\theta) = \frac{A}{3Q} \left[\frac{1}{2} \ln \frac{1 - \theta^3}{(1 - \theta)^3} - 3^{1/2} \operatorname{tg}^{-1} \left(\frac{2\theta + 1}{3^{1/2}} \right) \right]$$

The shape of the curve obtained by plotting Y^{-1} as a function of the product $Q\phi$ is quite simple (Figure 39b).

Thus it has been shown that the relaxation time for the hydrodynamic layer is short in comparison with that of the diffusion layer. Indeed, a rotation of the electrode of only two radians is sufficient to establish the hydrodynamic layer whereas the concentration profile settles much more slowly.

5.5.3. Sinusoidal Modulation of the Rotation Speed^(122,123)

Two types of modulation have been proposed, i.e.,

$$\begin{aligned} \Omega^{1/2} &= \Omega_0^{1/2} (1 + \varepsilon \cos \omega t) \\ \Omega &= \Omega_0 (1 + \varepsilon \cos \omega t) \end{aligned} \quad (306)$$

The current response to the latter is

$$I = \bar{I} + \Delta I_1 \cos(\omega t - \phi_1) + \Delta I_2 \cos(2\omega t - \phi_2) + \dots \quad (307)$$

where $\bar{I}$ is the d.c. current for a constant rotation speed Ω_0 . However, only the first order term has been studied. This corresponds to a first-order approximation valid when the amplitude of the modulation is small (linear case).

In the equation of convective diffusion [Eq. (296)] only the normal component v_z of the fluid velocity v has an influence. Using the expansion of v_z as a function of z given in Reference (123), a solution of Fick's equation can be found. This equation has been solved numerically⁽¹²²⁾ on the one hand and on the other using a semi-analytical expression of the form⁽¹²³⁾:

$$\frac{\Delta I_1}{\Delta \Omega} = \frac{\bar{I}}{\Omega_0} \left(A - j \frac{2DB}{\omega} \right) \quad (308)$$

which defines an electrohydrodynamical impedance

$$\frac{1}{Z_{\text{ehd}}} = \frac{\Delta I_1}{\Delta \Omega} \quad (309)$$

with

$$A = \frac{1}{2} \frac{\sum_{j=1}^n a_j (\omega/\Omega_0)^{2j}}{\sum_{j=1}^m b_j (\omega/\Omega_0)^{2j}} \quad \text{and} \quad B = \frac{1}{4D} \frac{(\omega/\Omega_0)^2 \sum_{j=1}^k c_j (\omega/\Omega_0)^{2j}}{\sum_{j=1}^l d_j (\omega/\Omega_0)^{2j}} \tag{310}$$

a_j , b_j , c_j and d_j are functions of Schmidt's number (ν/D).

For $n = k = 2$ and $m = l = 3$ there is good agreement between calculated values and measured values of Z_{ehd} in the case of Schmidt's numbers lower than 2100 and (ω/Ω_0) ranging from 0 to 10. This expression of Z_{ehd} is also in agreement with the numerical integration within the range of (ω/Ω_0) calculated (between 0 and 1). In order to obtain an expression of Z_{ehd} valid for higher Schmidt's numbers, it would be necessary to take account of terms of higher order.

Figure 40 shows the electrohydrodynamical impedance Z_{ehd} in the complex plane measured using the experimental set-up given in Figure 41, at different rotation speeds. The low frequency limit is equal to

$$\frac{dI_d}{d\Omega} (\omega/\Omega_0 \rightarrow 0) = \frac{1}{2} \frac{I_d}{\Omega_0} = \frac{1}{2} \frac{d}{\Omega_0^{1/2}} \tag{311}$$

since the limiting diffusion current I_d is equal to

$$I_d = d\Omega_0^{1/2} \tag{312}$$

Equations (311) and (312) allow one to determine d and hence the parameters defining the limiting diffusion current⁽²³⁾.

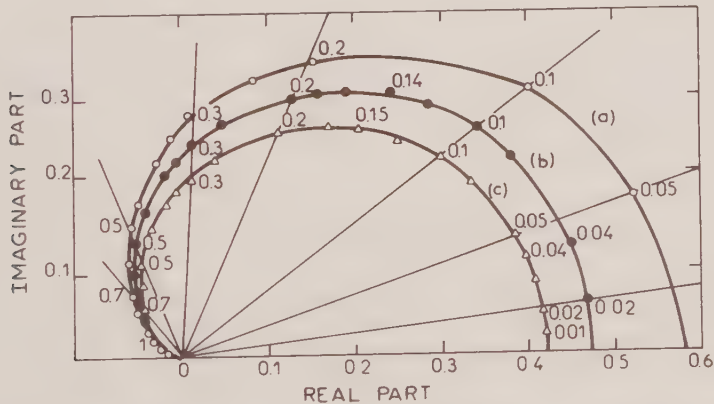


Figure 40. Electrohydrodynamical impedance $Z_{\text{ehd}}(\omega)$ in the complex plane at three rotation speeds of the rotating disk: curve (a) 600 rpm; (b) 900 rpm; (c) 1200 rpm, obtained in a solution of KCl (1 M), $\text{Fe}(\text{CN})_6\text{K}_3$ (10^{-3} M), $\text{Fe}(\text{CN})_6\text{K}_4$ (10^{-3} M). The straight lines show that the diagrams are homothetic. The numbers indicate the reduced frequencies in ω/Ω_0 [from Reference (123)].

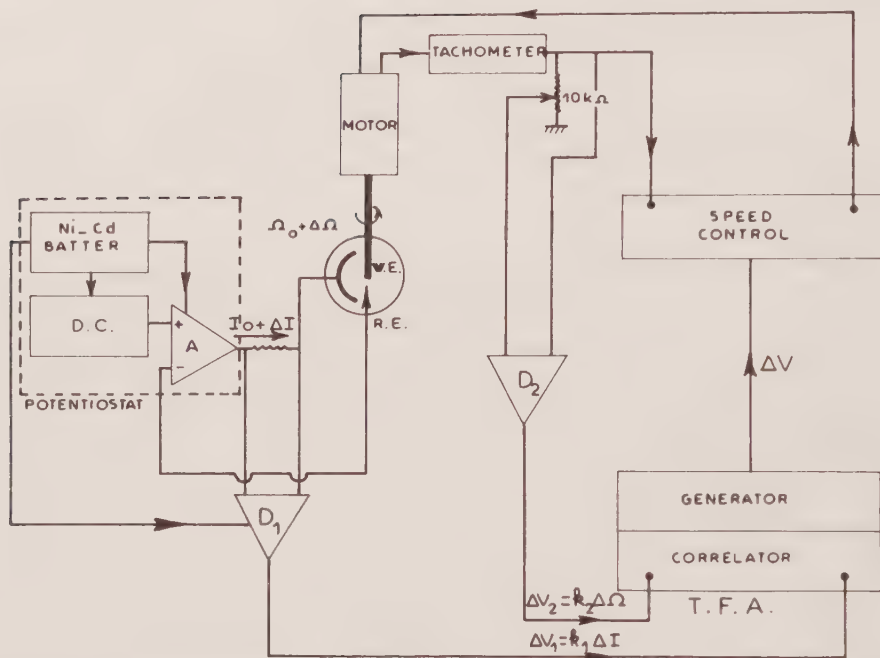


Figure 41. Experimental set-up devised for measuring the electrohydrodynamical impedance. D.C.: direct current source; A: operational amplifier; D_1 , D_2 : differential amplifiers; W.E.: working electrode; R.E.: reference electrode; T.F.A.: transfer function analyzer [from Reference (123)].

Analysis of the electrochemical impedance allows one to extract the diffusion component from an overall current, even if the latter is zero (Figure 42), and to determine Schmidt's number.

The studies performed hitherto have dealt with the limiting diffusion current, but it seems that application of this technique to processes controlled by both diffusion and charge transfer presents problems which remain unsolved.

6. Other Non-steady State Techniques

6.1. Analysis of Oscillating Electrochemical Systems

Oscillating electrochemical systems have been the subject of numerous investigations. The first case of periodicity was described by Fechner as early as 1828 in the case of the deposition and dissolution of silver in silver nitrate solution. However, a general criterion for the occurrence of oscillations was established only in 1955 by Bonhoeffer,⁽¹²⁵⁾ who studied the system of two autonomous equations $dx/dt = P(x, y)$ and $dy/dt = Q(x, y)$. He concluded that the presence of an autocatalytic step is necessary to initiate and maintain

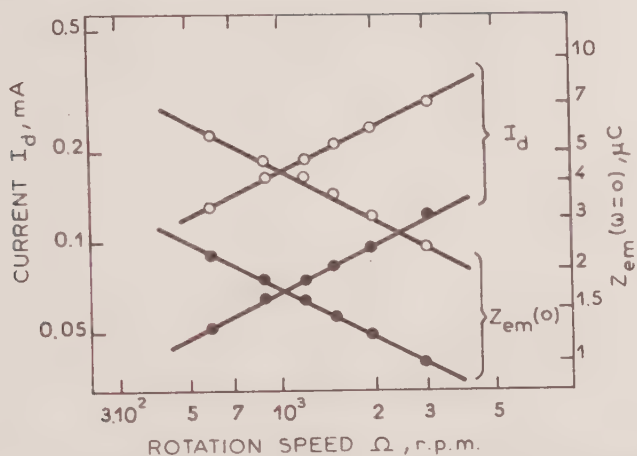


Figure 42. Variation of the diffusion part of the current I_d , deduced from measurements of the electrohydrodynamical impedance $Z_{\text{chd}}(\omega)$, as a function of the rotation speed Ω . Johnson-Matthey iron electrode ($A = 0.2 \text{ cm}^2$); electrolyte: aerated H_2SO_4 , 1 N; temperature: $25 \pm 0.2^\circ\text{C}$. (●) overall current = 0; (○) overall current = 1 mA [from Reference (124)].

the oscillations. However, it appears that the first electrochemical model taking account of mass transport has been proposed by Franck and Fitzhugh in 1961.⁽¹²⁶⁾ Subsequently Degn⁽¹²⁷⁾ and Szpak and Rice⁽¹²⁸⁾ also considered mass transport in the models they proposed. More recently, Wojtowicz⁽¹²⁹⁾ has reviewed the electrochemical oscillating systems related to anodic processes involving metals, as well as the anodic oxidation of non-metal compounds, to cathodic processes, to non-aqueous solutions, and to electric osmosis. The general conclusion is that electrochemical systems, which are systems open to matter and energy fluxes, can exhibit oscillations due to the complex couplings which exist between the various elementary processes taking place at the electrochemical interface, such as charge transfer, mass transport, etc.

6.1.1. Influence of the Regulation Device on Oscillating Systems

In many cases, oscillating systems have been considered as anomalies or peculiarities. If oscillations are to be dealt with in a non-steady state analysis technique, one must be very careful, because analysis of the oscillations is often difficult to interpret quantitatively. In some cases, qualitative interpretations have been advanced, but elaboration of an electrochemical model to interpret oscillations is generally very difficult. The reproducibility of experimental data is rather poor because the frequency and amplitude of the oscillations are very sensitive to very small changes of the initial and boundary conditions of the equations describing the system. When possible, it would be more advisable to try to stabilize the system, whatever scheme is used to study it.

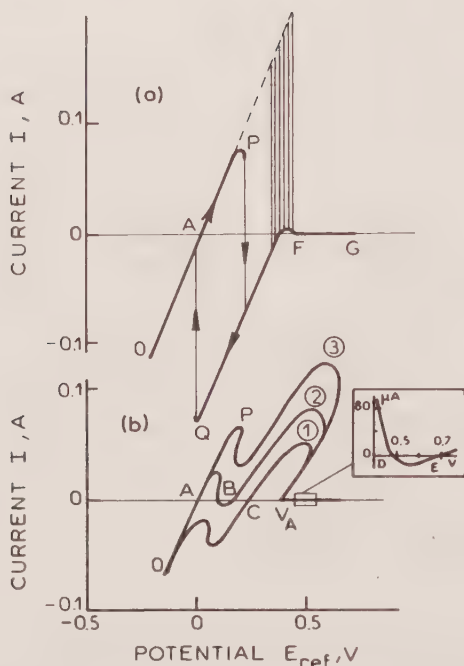


Figure 43. Polarization curves of iron in 12 *N* HNO₃ [from Reference (130)]. (a) Curve plotted using a potentiostat (at point F, oscillations appear) for $\Omega = 1600$ rpm. (b) Curve plotted using a negative impedance regulation for various rotation speeds of the electrode Ω : (1) 400 rpm, (2) 900 rpm, (3) 1600 rpm.

A great number of the oscillations described in the literature can doubtless be attributed to a bad choice of the regulation (misfitting of the load-line, filtering, etc.) since the oscillations are of course very sensitive to the characteristics of the polarization and measurement circuits. Thus, by using a potentiostat it has been possible to show the existence of a stable negative slope instead of the oscillations often observed with potentiometric regulation (Figure 1a). The behavior of iron in nitric acid is quite a striking example from this standpoint as shown in Figure 43. Using a negative internal resistance regulation, a stable polarization curve has been obtained (Figure 43b) instead of the oscillations over the whole potential range observed when using a potentiostat (Figure 43a)⁽¹³⁰⁾.

However, certain systems can be regarded as actually oscillating and must be studied from this standpoint. Indeed, the differential equations describing the electrochemical system can accept periodic solutions under certain conditions. But investigation of these solutions for non-linear systems is generally of high complexity. We shall briefly recall some general considerations on the stability of such systems.

6.1.2. General Considerations on the Stability of a Non-linear System⁽¹³¹⁾

In order to study the stability of a non-linear system, it is necessary to study the stability of the linearized system at every working point. If the

linearized system is stable (or unstable), then the non-linear system will be stable (or unstable) at a given working point. If the linearized system is unstable, the evolution of the system beyond the onset of the instability can lead to various types of behavior: i.e., sustained oscillations, divergent oscillations, relaxation oscillations, commutation towards another state, etc. These behaviors are often difficult to predict, but constitute the subject of the investigation of oscillating systems.

6.1.2.1. Stability of the Linearized System

As a first step, it is consequently necessary to find the conditions at which the equivalent linear system becomes unstable at a given working point of the non-linear system studied. For example, let us consider a system whose behavior is described by the following equations⁽¹³²⁾:

$$\frac{\partial c_i}{\partial t} = f_i(c_p, E) + D_i \nabla^2 c_i \quad (313)$$

$$\nabla^2 E = 0 \quad (314)$$

which are a special form of the general equations (10) and (11). In Eq. (313), the function $f_i(c_p, E)$ describes either the homogeneous kinetics, and is then independent of potential E (c_j is then a bulk concentration), or the heterogeneous kinetics, and depends in that case on the potential E (c_j is then a surface concentration). In the latter case, the second term in Eq. (313) expresses the surface diffusion of species i . In addition, the distribution of the potential E and the bulk concentration are subjected to boundary conditions at the interface determined by the rate constants of the heterogeneous reactions and by the current density.

6.1.2.1.1. Analytical Analysis of the Stability. It is clear that a mathematical discussion of the existence of instabilities is extremely difficult when the general case is to be considered. But it is possible to establish conditions at which the electrochemical system exhibits an instability leading to an oscillating behavior.

In the absence of chemical reactions in the electrolyte and expressing the surface concentrations of species i and j by the fractional coverage θ_i , θ_j , Eq. (313) becomes Eq. (315) if the species having a concentration c diffuse in the z -direction, and Eq. (316) if the species having a fractional coverage θ_i diffuse on the surface in the r -direction:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} \quad (315)$$

$$\frac{\partial \theta_i}{\partial t} = f_i(\theta_i, c_s, E) + D_i \frac{\partial^2 \theta_i}{\partial r^2} \quad (316)$$

where D and D_i are bulk and surface diffusion coefficients, respectively.

The current density $j_F(\theta_i, c_S, E)$, where c_S is the concentration c on the electrode surface, is governed by electrochemical reactions. For very small changes, denoted by Δ , the variations of the local quantities $\theta_i(r)$, $c_S(r)$, $E(r)$, $j_F(r)$, and $j(r)$, where j is the overall current density, are expressed by the following equations.

If two species of fractional coverage θ_1 and θ_2 diffuse on the surface, the equation system is:

$$\frac{\partial \Delta c}{\partial t} = D \frac{\partial^2 \Delta c}{\partial z^2} \quad (317)$$

$$\frac{\partial \Delta \theta_1}{\partial t} = A_1 \Delta \theta_1 + B_1 \Delta \theta_2 + F_1 \Delta c_S + G_1 \Delta E + D_1 \frac{\partial^2 \Delta \theta_1}{\partial r^2} \quad (318)$$

$$\frac{\partial \Delta \theta_2}{\partial t} = A_2 \Delta \theta_1 + B_2 \Delta \theta_2 + F_2 \Delta c_S + G_2 \Delta E + D_2 \frac{\partial^2 \Delta \theta_2}{\partial r^2} \quad (319)$$

$$\Delta j_F = a \Delta \theta_1 + b \Delta \theta_2 + f \Delta c_S + g \Delta E \quad (320)$$

$$\Delta E_{\text{ref}} = \Delta E + R_e \Delta j \quad (321)$$

$$\Delta j = C_d \frac{\partial \Delta E}{\partial t} + \Delta j_F \quad (322)$$

Equations (321) and (322), in which R_e and C_d denote the local values of the electrolyte resistance and of the double-layer capacity approximate for Eq. (314). Solutions of the equation system (Eqs. 317–322) are to be found as periodic functions of time and space (having a wavenumber $\bar{\nu}_i$) of the form:

$$\Delta \theta_i = \Delta \theta_i^0 \exp[j(\omega t + \bar{\nu}_i r)] \quad (323)$$

If diffusion is assumed to take place through a Nernst layer of thickness δ_N , we see that the relation between the variations Δj_F and Δc_S is, by Eq. (83)

$$\Delta c_S = -\frac{\delta_N}{nFD} \frac{\tanh(j\omega\delta_N^2/D)^{1/2}}{(j\omega\delta_N^2/D)^{1/2}} \cdot \Delta j_F = -N \Delta j_F \quad (324)$$

After eliminating Δj_F , ΔE , and Δc_S between Eqs. (318–322), and Eq. (324) one obtains:

$$(j\omega - A_1 - aP_1 + \bar{\nu}_1^2 D_1) \Delta \theta_1 - (B_1 + bP_1) \Delta \theta_2 = (G_1 + gP_1) \frac{R'_e}{R_e} \Delta E_{\text{ref}} \quad (325)$$

$$-(A_2 + aP_2) \Delta \theta_1 + (j\omega - B_2 - bP_2 + \bar{\nu}_2^2 D_2) \Delta \theta_2 = (G_2 + gP_2) \frac{R'_e}{R_e} \Delta E_{\text{ref}} \quad (326)$$

$$\begin{aligned} \Delta j - \frac{aR'_e/R_e}{1 + Nf + gR'_e} \Delta \theta_1 - \frac{bR'_e/R_e}{1 + Nf + gR'_e} \Delta \theta_2 \\ = \frac{R'_e}{R_e^2} \left(\frac{fR'_e}{1 + Nc + gR'_e} + \frac{R_e}{R'_e} - 1 \right) \Delta E_{\text{ref}} \end{aligned} \quad (327)$$

where

$$P_i = \left(\frac{F_i N + G_i R'_e}{1 + fN + gR'_e} \right) \quad \text{and} \quad R'_e = \frac{R_e}{1 + j\omega R_e C_d}$$

The electrochemical system will oscillate with a frequency $\omega/2\pi$, if the determinant

$$\begin{vmatrix} 0 & j\omega - A_1 - aP_1 + \bar{v}_1^2 D_1 & -(B_1 + bP_1) \\ 0 & -(A_2 + aP_2) & j\omega - B_2 - bP_2 + \bar{v}_2^2 D_2 \\ 1 & -\frac{aR'_e/R_e}{1 + fN + gR'_e} & -\frac{bR'_e/R_e}{1 + fN - gR'_e} \end{vmatrix} = 0 \quad (328)$$

The whole set of parameters satisfying this relation at $\omega = 0$ determines the appearance of multiple steady states.

6.1.2.1.2. Graphical Analysis of the Stability. A graphical analysis of the linear stability can be performed using Nyquist's theorem counting the number of poles P and rotations T , about the origin, of the impedance of the system plotted in the complex plane.⁽¹³³⁾ A good example of this analysis is the case of the iron-nitric acid interface which is known to exhibit spontaneous passivation.⁽¹³⁴⁾ In stabilizing the system as described above (Figure 43) and examining the impedance measured, it has been shown that the impedance is characteristic of an unstable system where oscillations are observed (Table 3).

6.1.2.2. Behavior of the System beyond the Onset of Instability

A general study of this problem is difficult, but in the simple case where the system is described by the following equation:

$$\frac{dx}{dt} = P(x, y) \quad \text{and} \quad \frac{dy}{dt} = Q(x, y) \quad (329)$$

a detailed study has been performed. As previously, the linearized system is studied about a working point defined by $P(x_0, y_0) = Q(x_0, y_0) = 0$ so that:

$$\frac{d}{dt} \begin{bmatrix} \Delta x \\ \Delta y \end{bmatrix} = \mathcal{A} \begin{bmatrix} \Delta x \\ \Delta y \end{bmatrix} \quad \text{with} \quad \mathcal{A} = \begin{bmatrix} A & B \\ C & D \end{bmatrix} \quad (330)$$

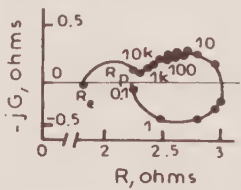
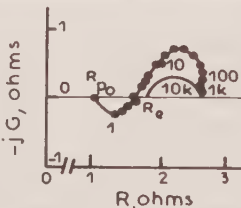
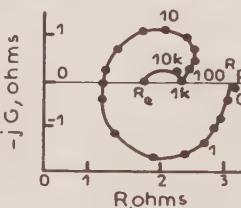
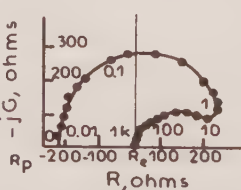
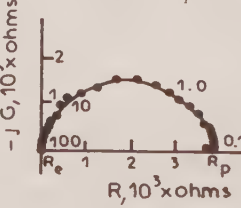
Stability is determined by the properties of the eigenvalues q_1 and q_2 of the matrix which are the roots of the characteristic equation:

$$\begin{vmatrix} A - q & C \\ B & D - q \end{vmatrix} = 0 \quad (331)$$

The properties of the roots fix the character of the equilibrium point (Table 4).

Thus, the properties of stability can generally be deduced from Eq. (329). It is then necessary to perform a detailed study of the trajectory of point $M(x, y)$ either by an analytical or numerical integration or by an isoclinical method.

Table 3
Impedances Measured at Points A, B, C, D, and E of Figure 43. Discussion of the Stability of the Electrochemical System^a

Polarization Point	Impedances	T	P	N	Potentiostat	Galvanostat
A		0	0	0	stable	stable
B		0	1	1	unstable	unstable
C		0	1	1	unstable	unstable
D		1	1	0	stable	unstable
E		0	0	0	stable	stable

^a From Reference (134).

Table 4
Different Cases Arising in Stability Analysis^a

Property of roots	Character of equilibrium point	Typical shape of trajectories
Real $q_1 \leq q_2 \leq 0$	Stable node	
$0 < q_1 \leq q_2$	Unstable node	
$q_1 < 0 < q_2$	Saddle	
Complex $\text{Re}(q) < 0$	Stable focus	
$\text{Re}(q) > 0$	Unstable focus	
$\text{Re}(q) = 0$	Center	

^a From Reference (129).

If a closed trajectory is found for M (limit cycle), the conclusion will be that the system will accept periodic solutions.

If a spiral is found, when it is convergent, it will indicate damped oscillations, hence a stable system, and when it is divergent, it will indicate diverging oscillations, hence an unstable system. However, trajectories can rarely be obtained except when using analog or digital methods.

In addition, many electrochemical systems exhibit, under certain conditions, a periodic behavior which cannot be described by continuous and differentiable equations. Such oscillations are called relaxation oscillations and have the form of a succession of analytical arcs and discontinuous jumps. It is assumed that these jumps can occur provided that there are no discontinuous changes of the energy stored in the system, for this would require a supply of infinite power.

6.1.3. Examples of Electrochemical Oscillating Systems

Although the systems investigated hitherto are mainly those for which certain parameters oscillate with time, there are others that can be classified as oscillating systems. These systems exhibit sustained spatio-temporal structures.

6.1.3.1. Multi-steady State Systems

Systems commutating from one state to another can be considered as oscillating systems, since a commutation can be regarded as the limit of an oscillation when its frequency tends to zero. We have seen examples of such multi-steady state systems in section 1.1 (Figure 1).

6.1.3.2. Space Oscillations

Systems presenting spatial periodicities, which are therefore qualified as dissipative structures, can also be considered as oscillating systems.

Such a space-structure appears in the case of zinc electrocrystallization in a Leclanché-cell medium.⁽¹³⁶⁾ Assuming that the adions diffuse at the surface of the electrode towards growth sites where they incorporate into the metal lattice, it has been shown that the current density is non-uniform and periodic (Figure 44). These current distributions can explain the spongy, compact, and dendritic deposits, which can be observed microscopically at low, medium and high average current densities, respectively.

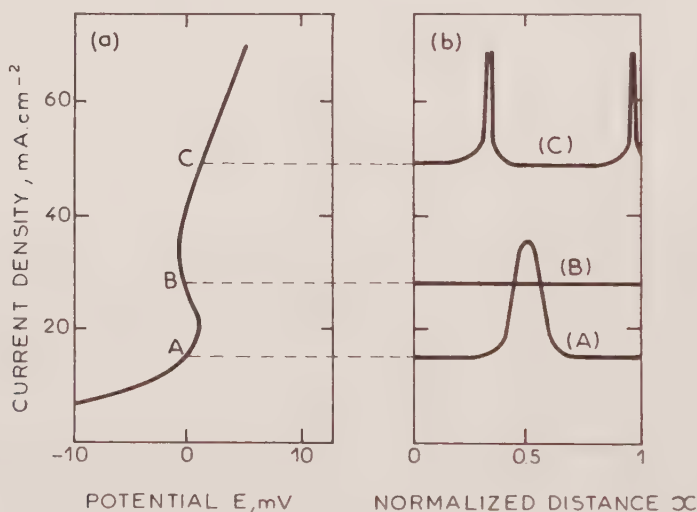


Figure 44. Non-uniform distribution of current in the case of zinc in Leclanché cell medium. (a) Current density-potential curve. (b) Distribution of the current in the z-direction on the electrode surface calculated at points A, B, and C of the polarization curve (a) [from Reference (136)].

6.1.3.3. Time Oscillations

Observation of time oscillations is performed by using a graphical recorder for slow oscillations or an oscilloscope (with or without storage) for rapid oscillations. We shall present two examples of time oscillations. The first one concerns ethylene oxidation and the second one the reduction of hydrogen peroxide.

6.1.3.3.1. *Oscillations Observed during Ethylene Oxidation.* Wojtowicz and Conway^(137,138) have proposed a model for the oxidation of ethylene on platinum during which oscillations of the electrolysis current are observed. According to this model ethylene diffuses through a layer of thickness δ_N towards the electrode at which it adsorbs and reacts with chemisorbed oxygen. If θ_E and θ_{OH} are the fractional coverages of ethylene and adsorbed hydroxyl ion arising from water molecules, k_E and k_{OH} the adsorption rate constants, and p the partial pressure of ethylene, we can write, assuming that adsorption obeys Langmuir's isotherm, that:

$$\frac{\theta_E}{1 - \theta_E - \theta_{OH}} = k_E p \quad (332)$$

$$\frac{\theta_{OH}}{1 - \theta_E - \theta_{OH}} = k_{OH} \exp\left(\frac{F}{RT} E\right) \quad (333)$$

Hence

$$\theta_E = \frac{k_E p}{1 + k_E p + k_{OH} \exp\left(\frac{F}{RT} E\right)} \quad (334)$$

and

$$\theta_{OH} = \frac{k_{OH} \exp\left(\frac{F}{RT} E\right)}{1 + k_E p + k_{OH} \exp\left(\frac{F}{RT} E\right)} \quad (335)$$

If the rate-determining step is the bimolecular oxidation of the chemisorbed species derived from ethylene, i.e.,



one has $I_F = k\theta_E\theta_{OH}$ and hence

$$I_F = \frac{kk_E p k_{OH} \exp\left(\frac{F}{RT} E\right)}{\left[1 + k_E p + k_{OH} \exp\left(\frac{F}{RT} E\right)\right]^2} \quad (337)$$

Now, the surface concentration c_S of ethylene is proportional to its partial pressure p . Consequently one has to solve Fick's equation, taking as boundary conditions:

$$I_F = \frac{kk_2 k_E c_S}{(1 + k_2 + k_E c_S)^2} \quad \text{where } k_2 = k_{OH} \exp\left(\frac{F}{RT} E\right). \quad (338)$$

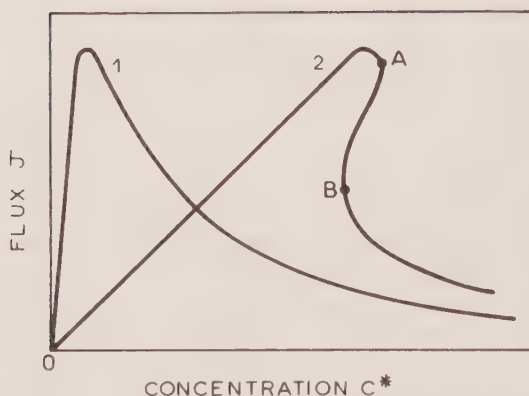


Figure 45. Curve $J = f(c^*)$ calculated using Eq. (340) in the case of $kk_E/D = 0$ (i.e., $D \rightarrow \infty$ without diffusion control) for curve 1, and $kk_E/D \geq 108$ for curve 2 where three values of the flux exist at the same c^* (multi-steady state system) [from Reference (138)].

Solving Fick's equation under such conditions is very difficult, but the steady state solution can be readily obtained assuming that diffusion occurs linearly in a diffusion layer of thickness δ_N , that is to say that the flux J of ethylene is equal to

$$J = D \frac{(c^* - c_s)}{\delta_N} \quad \text{for } z < \delta_N \quad (339)$$

Therefore, by eliminating c_s between Eqs. (338) and (339) since $I_F = nFAJ$, the following third-order equation can be established

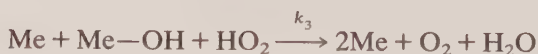
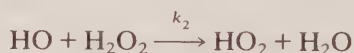
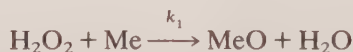
$$\alpha J^3 + \beta J^2 + \gamma J + \varepsilon = 0 \quad (340)$$

the coefficients $\alpha, \beta, \gamma, \varepsilon$ depending on the rate constants k_i and c^* . Figure 45 shows the shape of the $J = f(c^*)$ curve.

When $D \rightarrow \infty$ diffusion is very rapid and multiple steady states are no longer observed.

Investigation of the behavior of the system about the unstable points (branch AB in Figure 45) has shown that oscillations can be generated beyond these unstable points. This study is difficult in the case of ethylene oxidation but, in the following example, it has been possible to analyze the oscillations completely.

6.1.3.3.2. Oscillations Observed during the Catalytic Reduction of H_2O_2 .⁽¹³⁹⁻¹⁴¹⁾ In the case of the catalytic reduction of H_2O_2 on Cu_5FeS_4 , Tributch has proposed a reaction mechanism involving two autocatalytic reactions:





If we denote by X , Y , R , and A the concentrations of Me-OH , Me , H_2O_2 , and HO_2 , respectively, the system can be described by the following equations, since the current is due to the reduction of Me-OH which does not seem to participate in the oscillation process:

$$\frac{dX}{dt} = k_1 k_4 A R X - k_3 A X Y \quad (341)$$

$$\frac{dY}{dt} = k_6 A X Y - k_1 R Y \quad (342)$$

This Lotka-Volterra equation system is well known to lead to oscillatory behaviors. This system allows analytic integration and shows that copper and iron sulfides are periodically covered and uncovered by MeOH . Combining Eqs. (341) and Eq. (342) leads to:

$$k_3 A \left(\frac{dX}{dt} + \frac{dY}{dt} \right) - k_1 R \frac{d \ln X}{dt} - k_1 k_4 A \frac{d \ln Y}{dt} = 0 \quad (343)$$

Integration gives:

$$F(X, Y) = \exp[-n_3 A(X + Y)] X^{k_1 R} Y^{k_1 k_4 A R} = \text{constant} \quad (344)$$

The constant in Eq. (344) is determined by the initial and boundary conditions and gives the actual solution which can be compared to the observed oscillations (Figure 46). It should be noted that, strictly speaking, the oscillating phenomena are here of purely chemical nature. The electrode processes act as indicators of the Me-OH concentration change.

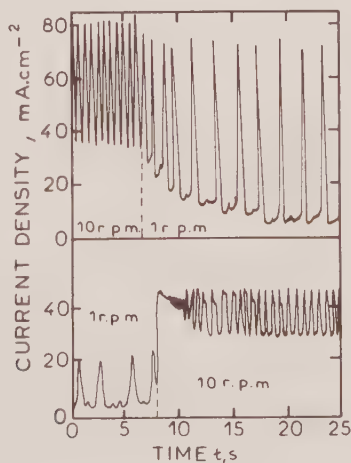


Figure 46. Influence of the electrode rotation speed on the oscillation frequency of Cu_5FeS_4 . Electrode potential: 0.6 V; electrolyte: $4 \times 10^{-1} \text{ M H}_2\text{O}_2$ [from Reference (139)].

6.2. Analysis of the Electrochemical Noise

Analysis of the spontaneous fluctuations (also called electrochemical noise), either of the current passing through an electrode or of the potential of an electrode, appears to be a powerful means for analyzing the elementary processes that control the passage of the current through an electrochemical interface. However, the use of this method presents some difficult problems both theoretically and experimentally.

From an experimental standpoint, there is a tremendous measurement problem. Indeed, one has to measure fluctuations of very small amplitude (some μV) superimposed on a constant steady state quantity, and moreover, this random signal is buried in a spurious noise which is also random. From a theoretical standpoint, difficult problems arise also because modeling involves the theory of stochastic processes in non-linear systems. Investigation of the electrochemical noise has been inspired, both experimentally and theoretically, by work relative to the physics of semiconductors.

Before describing the results obtained from analysis of electrochemical noise, we shall recall some definitions which can be useful in handling random signals.

6.2.1. General Considerations on Random Signals⁽¹⁴²⁾

A random signal $X(t)$ characterizes the evolution with respect to a parameter t (generally the time) of a system whose behavior is controlled by randomness. The set of n random variables $X_1(t), \dots, X_n(t)$ of n recordings allows one to define a statistical averaging at time t :

$$E[X(t)] = \lim_{n \rightarrow \infty} \frac{X_1(t) + \dots + X_n(t)}{n} \quad (345)$$

The time-averaging of the time evolution of a given sample $X_i(t)$ is:

$$\langle X_i(t) \rangle = \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T X_i(t) dt \quad (346)$$

For ergodic and stationary processes, one has:

$$E[X(t)] = \langle X_i(t) \rangle \quad (347)$$

independent of time. Similarly, the second-order moment corresponds, for ergodic and stationary processes, to the correlation function:

$$\psi_{XX}(\tau) = E[X(t)X(t+\tau)] = \langle X(t)X(t+\tau) \rangle, \quad (348)$$

the spectral density $\Psi_{XX}(\omega)$ or $\Psi_{XX}(s)$ being the Fourier or Laplace transform of the correlation function.

6.2.2. Instrumentation

Several techniques, based on spectral analysis,⁽¹⁴³⁾ have been used (Figure 47a), but the most adequate seems to be the correlation method (Figure 47b).^(26,144,152)

Let us assume that the signal of interest $e(t)$ is measured using two identical but independent channels (i.e., which have the same transfer function $A(s)$ but whose spurious noises, $n_1(t)$ and $n_2(t)$, are independent). In that case, it is possible to calculate the cross-spectral density of the outputs $x_1(t)$ and $x_2(t)$ of the two channels $\Psi_{x_1x_2}(s)$. Thus

$$\mathcal{L}x_1(s) = A(s)\mathcal{L}e(s) + \mathcal{L}n_1(s) \quad (349)$$

$$\mathcal{L}x_2(s) = A(s)\mathcal{L}e(s) + \mathcal{L}n_2(s) \quad (350)$$

Hence

$$\Psi_{x_1x_2}(s) = A(s)A(-s)\Psi_{ee}(s) + A(s)\Psi_{en_1}(s) + A(s)\Psi_{n_2e}(s) + \Psi_{n_1n_2}(s) \quad (351)$$

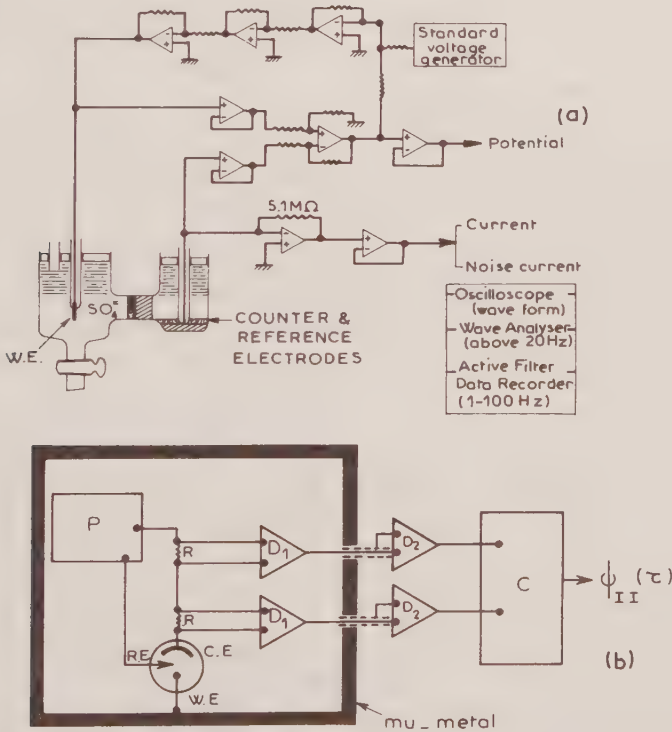


Figure 47. Electrochemical noise instrumentation. (a) Spectral analysis [from Reference (143)]. (b) Correlation technique [from Reference (152)]. P: potentiostat; R: resistance; D₁: preamplifier; D₂: amplifier; C: correlator; W.E.: working electrode; R.E.: reference electrode; C.E.: counter-electrode; $\psi_{II}(\tau)$ autocorrelation function of current noise.

Since the spurious noises and the signal to be measured are mutually independent one has

$$\Psi_{en_1}(s) = \Psi_{n_2e}(s) = \Psi_{n_1n_2}(s) = 0 \quad (352)$$

and hence

$$\Psi_{x_1x_2}(s) = A(s)A(-s)\Psi_{ee}(s) \quad (353)$$

Consequently, the autocorrelation function $\psi_{ee}(\tau)$ [or $\Psi_{ee}(s)$] of the noise analyzed can be obtained from the cross-correlation function $\psi_{x_1x_2}(\tau)$ [or $\Psi_{x_1x_2}(s)$] of the outputs of the two identical but independent channels whose input is the noise studied. This technique eliminates the influence of the spurious noises from the amplification channel (gain of about 10^6).

This theoretical calculation assumes that integration in Eq. (346) can be performed up to infinite time ($T \rightarrow \infty$) but since measurements are performed for a finite time, it is absolutely necessary to diminish the spurious noises as much as possible. To this end, the electrolysis cell, regulation, and amplifiers are enclosed in a shielding-box made of mu-metal acting as a Faraday cage. In addition Ni-Cd batteries are used to supply all the electronic devices.

6.2.3. Modeling of the Electrochemical Noise

6.2.3.1. Equivalent Circuit Approach

The first models of electrochemical noise were based on the results of Nyquist and Schottky:

- (a) Nyquist's theorem: at thermodynamic equilibrium, the potential of a dipole of impedance $Z(\nu)$ fluctuates in such a way that a bandwidth $(\nu_0, \nu_0 + \Delta\nu)$ contributes to the noise, by a source ΔE such that:

$$\overline{\Delta E^2} = 4kT \cdot \Delta\nu \cdot \text{Re}[Z] \quad (354)$$

where $\text{Re}[Z]$ denotes the real part of $Z(\nu_0)$, and k is Boltzmann's constant.

- (b) Schottky's theorem: a current I flowing through a diode fluctuates in such a way that a bandwidth $(\nu_0, \nu_0 + \Delta\nu)$ contributes to the noise (shot noise), by a source ΔI such that:

$$\overline{\Delta I^2} = 2eI\Delta\nu \quad (355)$$

where e is the electron charge.

Some authors tried to interpret noise measurements directly in terms of Nyquist's and Schottky's theorems (Figure 48).

These two theorems have long been used to elaborate models of the stochastic behavior of the interface. As a matter of fact, as was suggested by Barker,^(145,146) the behavior of the interface can be represented by an equivalent circuit with lumped or distributed components according to whether reaction processes or diffusion processes are considered (Figure 49). The

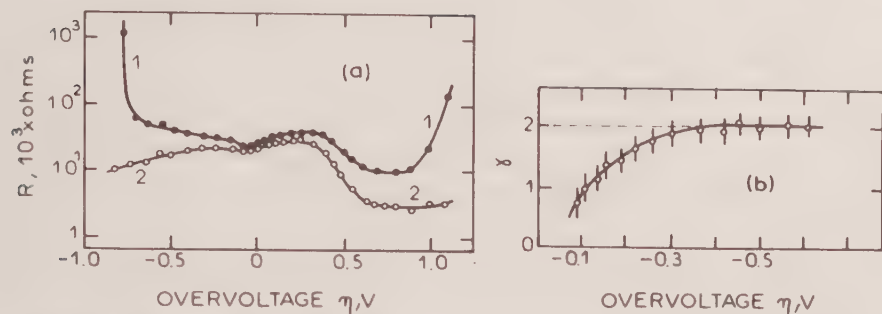


Figure 48. Two applications of Nyquist's and Schottky's theorems. Curve (a): potential dependence of the equivalent noise resistance (1) and the active component of impedance (2) of a Pt-disk electrode (diameter 0.18 mm); $\eta = E - E_{eq}$; $\nu = 800$ Hz; solution $0.05\text{ N Fe}^{2+}/\text{Fe}^{3+} + 2\text{ M H}_2\text{SO}_4$. Curve (b): potential dependence of the coefficient of shot noise γ defined by $\delta I^2 = \gamma eI$ during cathodic reduction of iodine on Pt (diameter 0.5 mm); $\nu = 1.8$ KHz; solution $0.02\text{ N KI}_3 + 0.5\text{ N KI} + 2\text{ N KCl}$ [from Reference (147)].

equivalent circuit is then treated as a linear electric network in order to obtain the overall noise across it.

6.2.3.2. The Langevin Method

A more microscopic approach can be performed using Langevin's method. This method was applied for the first time to the electrochemical interface by Tyagai.⁽¹⁴⁷⁻¹⁴⁹⁾ It consists of adding a random term to the state equations which describe the deterministic behavior of the interface. This will be exemplified in two different cases:

(a) In the case of two consecutive electrochemical reactions 1 and 2 coupled by an adsorbed intermediate of fractional surface coverage θ , as in the case of hydrogen evolution in the Volmer-Heyrovsky mechanism, we can

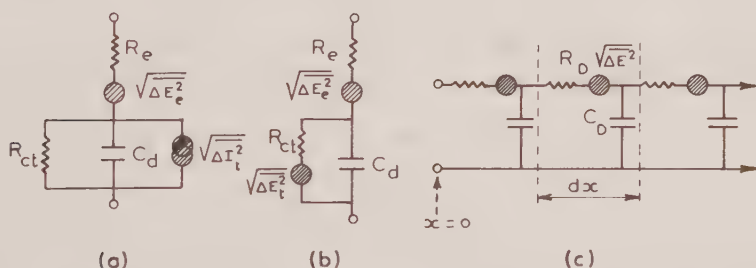


Figure 49. Equivalent noise circuits [from Reference (145)]. Equivalent noise generators (shaded circles) are associated with the resistances of the electrical equivalent circuit (see Figure 3) through Nyquist's theorem. (a) Potential- and current-noise generators for pure charge transfer; (b) potential-noise generators for pure charge transfer; (c) potential-noise generators for a diffusion-controlled process. The behavior of the diffusion layer is approximated by a transmission line with characteristic parameters R_D and C_D .

write, setting $\Delta I_F = \Delta I_1 + \Delta I_2$,

$$\Delta I_1 = \frac{\partial I_1}{\partial E} \Delta E + \frac{\partial I_1}{\partial \theta} \Delta \theta + \widetilde{\Delta I_1} \quad (356)$$

$$\Delta I_2 = \frac{\partial I_2}{\partial E} \Delta E + \frac{\partial I_2}{\partial \theta} \Delta \theta + \widetilde{\Delta I_2} \quad (357)$$

$$eN \frac{d\theta}{dt} = \Delta I_1 - \Delta I_2 \quad (358)$$

where $\widetilde{\Delta I_1}$ and $\widetilde{\Delta I_2}$ are the random perturbation sources and N is Avogadro's number.

Since the noise current is to be determined, it is necessary to impose $\Delta E = 0$. By Fourier transform one obtains:

$$\Delta I_F = \Delta \theta \left(\frac{\partial I_1}{\partial \theta} + \frac{\partial I_2}{\partial \theta} \right) + \widetilde{\Delta I_1} + \widetilde{\Delta I_2} \quad (359)$$

$$eNj\omega \Delta \theta = \Delta \theta \left(\frac{\partial I_1}{\partial \theta} - \frac{\partial I_2}{\partial \theta} \right) + \widetilde{\Delta I_1} - \widetilde{\Delta I_2} \quad (360)$$

By eliminating $\Delta \theta$ between Eqs. (359) and (360), one obtains:

$$\Delta I_F = \frac{1}{eNj\omega - \left(\frac{\partial I_1}{\partial \theta} - \frac{\partial I_2}{\partial \theta} \right)} \left[\widetilde{\Delta I_1} \left(eNj\omega + 2 \frac{\partial I_2}{\partial \theta} \right) + \widetilde{\Delta I_2} \left(eNj\omega - 2 \frac{\partial I_1}{\partial \theta} \right) \right] \quad (361)$$

Now, taking the quadratic mean, if $\Delta I_F = A\widetilde{\Delta I_1} + B\widetilde{\Delta I_2}$ the Fourier transform leads to:

$$\overline{\Delta I_F^2} = AA' \overline{\Delta I_1^2} + BB' \overline{\Delta I_2^2} \quad (362)$$

where A' and B' denote the conjugate quantities of the complex quantities A and B . Hence:

$$\overline{\Delta I_F^2} = \overline{\Delta I_1^2} \frac{\omega^2 e^2 N^2 + 4 \left(\frac{\partial I_2}{\partial \theta} \right)^2}{\omega^2 e^2 N^2 + \left(\frac{\partial I_2}{\partial \theta} - \frac{\partial I_1}{\partial \theta} \right)^2} + \overline{\Delta I_2^2} \frac{\omega^2 e^2 N^2 + 4 \left(\frac{\partial I_1}{\partial \theta} \right)^2}{\omega^2 e^2 N^2 + \left(\frac{\partial I_2}{\partial \theta} - \frac{\partial I_1}{\partial \theta} \right)^2} \quad (363)$$

In order to calculate the elementary noise sources $\widetilde{\Delta I_1}$ and $\widetilde{\Delta I_2}$, Tyagai applies an extended form of Schottky's theorem to each process, i.e., if subscript i denotes 1 or 2, one has:

$$\overline{\Delta I_i^2} = (I_{ia} + I_{ic})ne \quad (364)$$

if I_{ia} and I_{ic} are the anodic and cathodic parts of the current such that

$$I_i = I_{ia} - I_{ic} \quad (365)$$

Now, if R_{p_i} is the polarization resistance, one has:

$$\frac{1}{R_{p_i}} = \frac{\partial I_i}{\partial E} = \frac{ne}{kT} [(1 - \alpha)I_{ia} + \alpha I_{ic}] \quad (366)$$

In eliminating I_{ia} and I_{ic} between Eqs. (364), (365), and (366) one has:

$$\overline{\Delta I_i^2} - 4kTR_{p_i}^{-1} - 2ne(1 - 2\alpha)I_i \quad (367)$$

This value gives $\overline{\Delta I_1^2}$ and $\overline{\Delta I_2^2}$, and substituting into Eq. (363), the spectral density of the current noise $\overline{\Delta I_F^2}$ is obtained.

(b) If the electrochemical reactions are diffusion-controlled, one has:

$$\Delta I_F = \frac{\partial I_F}{\partial \theta} \widetilde{\Delta \theta} + \frac{\partial I_F}{\partial c} \widetilde{\Delta c_s} + \frac{\partial I_F}{\partial E} \widetilde{\Delta E} \quad (368)$$

Hence

$$\overline{\Delta I_F^2} = \left(\frac{\partial I_F}{\partial \theta} \right)^2 \overline{\Delta \theta^2} + \left(\frac{\partial I_F}{\partial c} \right)^2 \overline{\Delta c_s^2} + \left(\frac{\partial I_F}{\partial E} \right)^2 \overline{\Delta E^2} \quad (369)$$

$\overline{\Delta \theta^2}$ is calculated as previously. Tyagai has calculated $\overline{\Delta c_s^2}$ by assuming that the elementary fluctuations of the concentrations in a layer (z_i , $z_i + \Delta z$) at a distance z_i from the electrode surface are of the same form as with semiconductors, i.e.,

$$\overline{\Delta c^2}(z_i, \nu) = \frac{4c(z_i)\Delta z \Delta \nu}{D} \quad (370)$$

This local fluctuation $\widetilde{\Delta c}(z_i, \nu)$ decreases exponentially up to the interface, according to Fick's equation, to give a contribution

$$\overline{\Delta c_{z_i}^2}(0, \nu) = \overline{\Delta c^2}(z_i, \nu) \exp[-z_i(2\omega/D)^{1/2}] \quad (371)$$

If the diffusion layer is sliced into N equal parts of thickness Δz the fluctuation $\overline{\Delta c_s^2} = \overline{\Delta c^2}(0, \nu)$ at the electrode surface is obtained by adding the effects of all the slices, i.e.,

$$\overline{\Delta c^2}(0, \nu) = \sum_{i=1}^N \overline{\Delta c^2}(z_i, \nu) \exp[-z_i(2\omega/D)^{1/2}] \quad (372)$$

Replacing the sum by an integral, it turns out in the case of a diffusion layer of infinite thickness that:

$$\overline{\Delta c^2}(0, \nu) = 4\Delta \nu \left[\frac{c(0)}{(2\omega D)^{1/2}} - \frac{I_F}{2\omega neD} \right] \quad (373)$$

Transferring $\overline{\Delta \theta^2}$ and $\overline{\Delta c^2}(0, \nu)$ into Eq. (369), the spectral density of the current noise (with $\Delta E = 0$) or of the potential noise (with $\Delta I = 0$) can be

obtained. This method involves a difficulty inherent to Langevin's method itself since the definition of the elementary sources is always very difficult. Tyagai has adopted the results obtained with semiconductors, but it would seem more satisfactory to define the elementary sources in terms of a more microscopic theory of the processes involved at the interface.

6.2.3.3. Noise Generated by Flux Fluctuations

Thornber⁽¹⁵⁰⁾ and subsequently Blanc *et al.*⁽¹⁵¹⁾ have assumed that the elementary (hence independent) fluctuations are a consequence of fluctuations of the flux of matter provided by reaction or diffusion, due to the fact that the nature of matter is discrete. They assumed that each flux $J_i(t)$ can be expressed by:

$$J_i(t) = \langle J_i(t) \rangle + \Delta J_i(t) + d_i(t) \quad (374)$$

The term $\Delta J_i(t)$ represents the part of the fluctuations induced under the influence of the elementary source $d_i(t)$ which is a Poisson process such that:

$$\langle d_i(t) \rangle = 0 \quad (375)$$

$$\langle d_i(t) d_i(t - \tau) \rangle = \langle J_i(t) \rangle \delta(\tau) \quad (376)$$

$$\langle d_i(t) d_j(t - \tau) \rangle = 0 \quad (377)$$

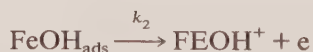
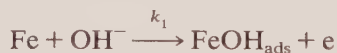
$\Delta J_i(t)$ satisfies macroscopic equations and is such that $\langle \Delta J_i(t) \rangle = 0$.

Blanc *et al.* showed that the Langevin-type elementary sources used by Tyagai are deduced from $d_i(t)$ using a matrix relationship:

$$\ell(t) = \mathbf{L} \mathbf{d}(t) \quad (378)$$

the components of $\ell(t)$ being the $\widetilde{\Delta I_1}$, $\widetilde{\Delta I_2}$, $\widetilde{\Delta C_S}$ terms used by Tyagai and $\mathbf{d}(t)$ the vector whose components are $d_i(t)$.

A rigorous microscopic definition of the noise sources used by Tyagai can thus be established. This was illustrated by calculating the noise resulting from the anodic dissolution of iron in sulfuric acid medium (pH = 0) at low currents according to the well-known mechanism:



where the rate constants obey Tafel's equation: $k_i = k_{i0} \exp(b_i E)$. The FeOH^+ ion reacts in the solution bulk with the proton H^+ to give ferrous ion; the OH^- ion diffuses in the solution, but we shall assume that reactions at the interface are sufficiently slow so that OH^- diffusion can be neglected. In this case, the concentration of OH^- at the electrode is constant. It is also assumed that the concentration of Fe is constant.

If J_p and J_c denote the production and consumption fluxes of FeOH_{ads} , which covers a fraction θ of the electrode surface, i.e.:

$$J_p = k_1(1 - \theta)A \quad (379)$$

$$J_c = k_2\theta A \quad (380)$$

then:

$$A\beta \frac{d\theta}{dt} = (J_p - J_c) \quad (381)$$

Since the production or consumption of one FeOH corresponds to the transfer of one electron into the metal, the faradaic current is:

$$I_F = eA (J_p + J_c) \quad (382)$$

Steady state is reached when $d\theta/dt = 0$ and hence

$$\langle \theta \rangle = \frac{k_1}{k_1 + k_2}; \quad (383)$$

$$\langle I_F \rangle = 2eA \frac{k_1 k_2}{k_1 + k_2} \quad (384)$$

$$\langle J_p \rangle = \langle J_c \rangle = A \frac{k_1 k_2}{k_1 + k_2} \quad (385)$$

About a given polarization point, a very small variation, such that the system remains linear, leads to variations of $\Delta\theta$ and ΔE about $\langle \theta \rangle$ and $\langle E \rangle$ such that:

$$\Delta J_p = -k_1 \Delta\theta + \frac{k_1 k_2}{k_1 + k_2} b_1 \Delta E \quad (386)$$

$$\Delta J_c = k_2 \Delta\theta + \frac{k_1 k_2}{k_1 + k_2} b_2 \Delta E \quad (387)$$

The behavior of the state variables $\Delta\theta$ and ΔE is then governed by equations like Eq. (388):

$$\frac{d}{dt} \begin{bmatrix} \Delta\theta \\ \Delta E \end{bmatrix} = \begin{bmatrix} -\frac{k_1 + k_2}{\beta} & \frac{k_1 k_2 (b_1 - b_2)}{\beta} \\ \frac{e}{C_d} (k_1 - k_2) & -\frac{1}{C_d} \left[\frac{1}{R_e} + e \frac{k_1 k_2}{k_1 + k_2} (b_1 + b_2) \right] \end{bmatrix} \begin{bmatrix} \Delta\theta \\ \Delta E \end{bmatrix} + \begin{bmatrix} \ell_\theta(t) \\ \ell_E(t) \end{bmatrix} \quad (388)$$

with

$$\ell(t) = \begin{bmatrix} \ell_\theta(t) \\ \ell_E(t) \end{bmatrix} = [d_p(t) - d_c(t)] \begin{bmatrix} 1/\beta \\ -e/C_d \end{bmatrix} \quad (389)$$

The observation equation is:

$$y = \Delta I = -\frac{\Delta V}{R_e} \quad (390)$$

Under such conditions, one can calculate the correlation function $\psi_{II}(\tau)$ of the current

$$\psi_{II}(\tau) = \mathcal{C} \exp \mathcal{A} \tau \left[\int_0^\infty \exp(\mathcal{A} \mu) \cdot Q \cdot \exp(\mathcal{A}^T \mu) d\mu \right] \mathcal{C}^T \quad (391)$$

with

$$Q = \frac{2k_1 k_2}{k_1 + k_2} \begin{bmatrix} 1/\beta^2 & 0 \\ 0 & e^2/C_d^2 \end{bmatrix} \quad (392)$$

defined by

$$\psi_{ee}(\tau) = Q \delta(\tau) \quad (393)$$

and where $\mathcal{A}^T$ is the transposed matrix of the state matrix $\mathcal{A}$, defined by Eq. (26) and Eq. (388); $\mathcal{C}^T$ is the transposed matrix of the observation matrix $\mathcal{C}$ defined by Eq. (23) and Eq. (390); i.e.,

$$\mathcal{C} = [0 \quad -1/R_e] \quad (394)$$

The good agreement between the autocorrelation function measured and the one calculated by this method in the case of iron dissolution (Figure 50) leads to the conclusions: (i) that the electrochemical noise observed is induced by flux fluctuations which are a Poisson process and (ii) that the concepts used to calculate the electrochemical impedance also interpret the electrochemical noise. A similar conclusion has also been drawn in the case of the diffusion noise of ferricyanide ion when reduced on a platinum rotating disk electrode.

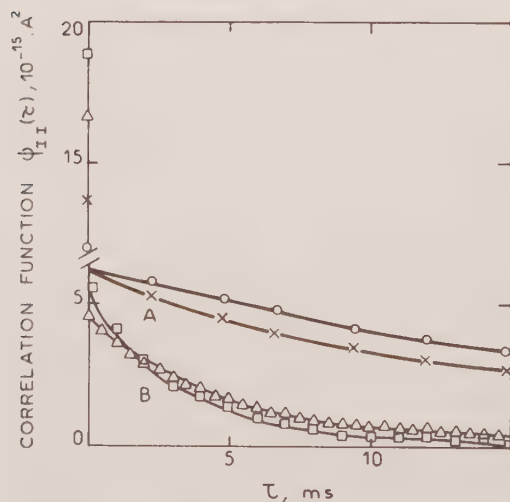


Figure 50. Electrochemical noise resulting from the anodic dissolution of iron in molar sulfuric acid as measured at two different current densities (rotating disk electrode, 0.5 cm in diameter, rotation speed 2000 rpm; temperature, 25°C). Curve A: Current density, 11.5 mA cm⁻²; (○) correlation function $\psi_{II}(\tau)$ calculated using the model proposed; (×) $\psi_{II}(\tau)$ measured experimentally. Curve B: Current density, 60 mA cm⁻²; (Δ) calculated $\psi_{II}(\tau)$; (□) measured $\psi_{II}(\tau)$. The values of parameters R_e , C_d , and K_i used for the numerical simulation were determined from impedance measurements [from Reference (151)].

6.2.3.4. Electrocrystallization Noise

Unlike the previous case, in the study of electrocrystallization it presently seems that in order to interpret the electrochemical noise one has to take account of processes which are not necessary to explain the deterministic behavior (e.g., impedance). As a matter of fact, as shown in Figure 51, the noise has a much more important value of $\psi_{II}(0)$ than in the cases mentioned above, and its current dependence is related to the structure of the deposit in contradiction to what happens with the impedance.⁽¹⁵²⁾

Since the concepts that allow one to explain the impedance are not sufficient to interpret the electrochemical noise in the case of electrocrystallization, some authors take account of the random nature of nucleation. Modeling the formation of clusters up to a critical size, leading to a stable nucleus, has been investigated only recently. Certain authors have proposed stochastic equations for the evolution of the number of particles in a cluster.^(153,154) Some others have considered a master equation describing a markovian process. They calculated the probability $P(i, t)$ of observing a cluster of size i at instant t and therefrom deduced

- (i) a nucleation rate inversely proportional to the time required by a nucleus to reach a critical size
- (ii) the critical number of adatoms that allows the growth of a crystallite.⁽¹⁵⁵⁾ It is generally considered that the formation of these critical nuclei follows a Poisson law.

In general, the model for the electrocrystallization noise is constructed assuming that the current obeys a law $I(t)$, due to the growth of a crystallite, which takes account of the instant of birth τ_i of the crystallite and also of its

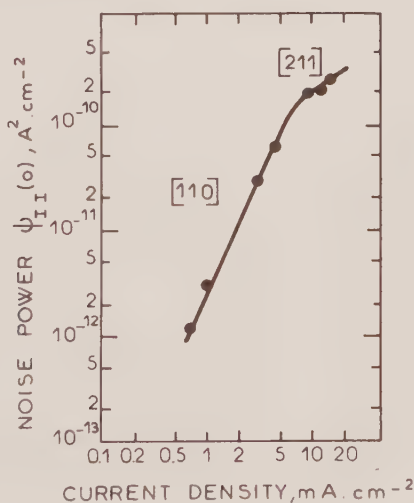


Figure 51. Electrocrystallization noise: Plot of the noise power $\psi_{II}(0)$ vs. average current density I , in the case of nickel electrodeposition in Watts electrolyte ($pH = 2.5$, temperature $50^\circ C$). For currents higher than about 10 mA cm^{-2} the orientation of the deposit is $[211]$ whereas for lower currents a $[110]$ orientation is observed [from Reference (152)].

lifetime " a " which can have a fixed or random value; in other words:

$$I(t) = g(t, \tau_p, a) \quad (395)$$

Two different approaches are here possible:

(i) Statistical averaging is calculated from the probability density

$$P(I) = \sum_{k=1}^K P(I/K)P(K) \quad (396)$$

where $P(K)$ is the Poisson law; $P(I)$ the probability for the current to have a value I ; $P(I/K)$ the conditional probability for the current to have a value I considering the growth of K crystallites. This analysis is particularly useful in studying the first steps of electrocrystallization.⁽¹⁵⁶⁾

(ii) In order to analyze the fluctuations of a steady state, it is possible to apply the theory of shot noise and calculate directly the average value and the correlation function $\psi_{II}(\tau)$ of the electrocrystallization noise which can be compared to measurements performed using a correlator.⁽¹⁵⁷⁾ Here, one has:⁽¹⁵⁸⁾

$$\langle I(t) \rangle = \int_{-\infty}^{+\infty} \langle g(t, \theta, a) \rangle_a \rho(\theta) d\theta \quad (397)$$

$$\psi_{II}(\tau) = \int_{-\infty}^{+\infty} \langle g(t, \theta, a)g(t - \tau, \theta, a) \rangle_a \rho(\theta) d\theta \quad (398)$$

where $\langle g \rangle_a$ represents an average value of g taken with respect to the random character of a ; $\rho(\theta)$ is the Poisson distribution density of the τ_p . When this distribution is stationary, then $\rho(\theta) = \rho = \text{a constant}$.

Glossary of Symbols

A	electrode area	(12)†
C_d	double-layer capacity	Fig. 3
c_i	concentration of species i	(11)
$\bar{c}_i$	concentration of species i for d.c. polarization	(71)
c_i^*	concentration of species i in the bulk of the solution	(38)
D	diffusion coefficient	(15)
$\mathfrak{D}$	Dawson's integral	(277)
E	potential	(10)
E°	standard potential	(33)
E_{eq}	equilibrium potential	(38)
E_{ref}	reference potential	(12)
$E[X(t)]$	statistical average of the random variable $X(t)$	(345)
$E_{1/2}$	half wave potential	(128)

† Numbers in parentheses refer to Equations.

E_z	potential of zero charge	(281)
e	electron charge	(355)
F	Faraday constant (96,500 C)	(1)
I_C	charging current of the double layer	(14)
I_F	faradaic current	(1)
I_l	limiting diffusion current	(138)
I_0	exchange current	(1)
$\hat{I}(t)$	convoluted current	(136)
J_i	flux of species i	(11)
j	imaginary symbol	(69)
k_f, k_i	rate constant of the forward reaction	(27)
k_b, k_{-i}	rate constant of the backward reaction	(27)
$\mathcal{L}$	Laplace operator	(44)
$N(\omega)$	$= \frac{\tanh[\delta_N(j\omega/D_O)^{1/2}]}{D_O(j\omega/D_O)^{1/2}}$	(83)
n	number of electrons	(1)
P	pressure	(12)
p	partial pressure	(332)
$Q(t)$	quantity of electricity	(179)
R	molar gas constant	(1)
R_{ct}	charge transfer resistance	(70)
R_e	electrolyte resistance	Fig. 3
R_p	polarization resistance	(146)
s	$=\sigma + j\omega$ Laplace variable	(44)
T	absolute temperature	(1)
$\langle X(t) \rangle$	time average of the random variable $X(t)$	(346)
$Z(\omega)$	impedance of the interface	(79)
z	normal distance from the electrode surface	(28)
$\operatorname{erfc} z$	definition of	(60)
α	transfer coefficient	(1)
β_i	maximum surface concentration of species i	(19)
Δ	small perturbation symbol	(68)
δ_N	thickness of the diffusion layer	(80)
$\zeta(x)$	$=\operatorname{erfc} x \exp x^2$	(161)
η	overvoltage	(1)
θ_i	surface coverage	(19)
λ	$=k_f/\sqrt{D_O} + k_b/\sqrt{D_R}$	(58)
ν	frequency	(354)
Ξ	$= \frac{1}{nFA} \left[\frac{1}{c_O^* \sqrt{D_O}} + \frac{1}{c_R^* \sqrt{D_R}} \right]$	(165)
σ	real part of the Laplace variable	(264)
$\psi_{XY}(\tau)$	correlation function of $X(t)$ and $Y(t)$	(348)
Ω	rotation speed of the electrode	(12)
ω	angular frequency	

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4

A.C. Techniques

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Notation

A list of symbols used in this chapter with their definitions can be found on page 287.

1. General Introduction

1.1. Linear Systems; Definition of Impedance

A *linear system* is defined as a system for which the response $y(t)$ to an applied perturbation $x(t)$ is determined by the differential equation⁽¹⁾

$$\begin{aligned} b_0 \frac{d^m y(t)}{dt^m} + b_1 \frac{d^{m-1} y(t)}{dt^{m-1}} + \dots + b_m y(t) \\ = a_0 \frac{d^n x(t)}{dt^n} + a_1 \frac{d^{n-1} x(t)}{dt^{n-1}} + \dots + a_n x(t) \end{aligned} \quad (1)$$

From this equation it follows that, if $x(t)$ is sinusoidal, e.g., an a.c. current

$$\Delta I = I_m \sin \omega t \quad (2)$$

then $y(t)$, e.g., the voltage response, must be sinusoidal too:

$$\Delta V = V_m \sin (\omega t - \phi) = V_m [\cos \phi \sin \omega t - \sin \phi \cos \omega t] \quad (3)$$

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The relation between ΔI and ΔV is completely determined by $V_m/I_m = |Z|$ and the phase angle ϕ , or by the two components Z' and Z'' of the vector Z :

$$Z' = |Z| \cos \phi \quad (4)$$

$$Z'' = |Z| \sin \phi \quad (5)$$

Sometimes it is convenient to express this relation in terms of the complex impedance Z , which is defined as the quotient of the Laplace transforms of ΔV and ΔI , with the imaginary Laplace parameter $i\omega$, ω being the angular frequency and $i = (-1)^{1/2}$. It is easily derived (see Appendix I) that

$$Z = \frac{\Delta \bar{V}(i\omega)}{\Delta \bar{I}(i\omega)} = Z' - iZ'' \quad (6)$$

1.2. Non-linear Systems

Generally an electrochemical cell is a non-linear system, primarily due to the exponential terms in the potential difference $E - E^\circ$, occurring in the current-voltage relation describing charge transfer. Starting from the sinusoidal current, cf. Eq. 2, ΔI being a small perturbation, the resulting potential response can be written in a Taylor expansion

$$\Delta E = (dE/dI)\Delta I + \frac{1}{2}(d^2E/dI^2)\Delta I^2 + \dots \quad (7)$$

Conversely, starting from a pure sinusoidal potential perturbation

$$\Delta E = V_m \sin \omega t \quad (8)$$

$$\Delta I = (dI/dE)\Delta E + \frac{1}{2}(d^2I/dE^2)\Delta E^2 + \dots \quad (9)$$

The quadratic terms, containing $\sin^2 \omega t = \frac{1}{2}(1 - \cos 2\omega t)$, give rise to a second harmonic and a d.c. (rectification) response. Further higher order terms lead to contributions of higher harmonics to the total response (see sections 3.2 and 4).

1.3. A.C. Techniques Applied to Electrochemical Cells

1.3.1. The Faradaic Process

In the most simple case, the relation between faradaic current and interfacial potential is determined by single electron charge transfer and mass transport. The former is described most generally by the rate equation for the current density $j_F = I_F/A$:

$$-j_F = nF \left\{ k_f \prod_{i=1}^M c_{O_i}(0, t) - k_b \prod_{j=1}^N c_{R_j}(0, t) \right\} \quad (10)$$

where c_{O_i} and c_{R_j} are the concentrations of the species involved in the reduction

and the oxidation, respectively, and

$$\ln (k_b/k_f) = (nF/RT)(E - E^\circ) = \varphi \tag{11}$$

The rate constants k_f and k_b are functions of potential, quite formally expressed by

$$\begin{aligned} (RT/nF)d(\ln k_f)/dE &= -\alpha \\ (RT/nF)d(\ln k_b)/dE &= 1 - \alpha \end{aligned} \tag{12}$$

where α , the *apparent* cathodic transfer coefficient, comprises all influences of potential (activation energy, double layer effects, etc.).

The differential equations and boundary conditions describing the transport process are less general, because their formulation depends on the geometry of the electrode and the hydrodynamic conditions of the experiment. In view of the field of application of a.c. techniques we have to consider the cases listed in Table 1 where in addition the accepted nomenclature for the appropriate theoretical models is mentioned.

Sometimes the solution of a particular transport problem is directly visible, but usually it is obtained via the method of Laplace transforms, which in first instance leads to a fairly simple linear relation(ship) between surface concentration and current density in the transformed notation.^(2,3)

$$\bar{c}(0, s) = f(s)\bar{j}_F(s) \tag{13}$$

and, after inverse transformation to the relation between $c(0, t)$ and j_F :⁽²⁸⁾

$$c(0, t) = c^* \pm \int_0^t j_F(u) \mathcal{L}^{-1} f(t-u) du \tag{14}$$

Table 1
Models for Diffusion Theory in Use for A.C. Techniques

Experimental conditions	Model
Unstirred solutions	Semi-infinite diffusion
Solid planar electrode	Stationary plane (linear diffusion)
Solid spherical electrode	Stationary sphere (spherical diffusion)
Hanging mercury drop electrode	Idem
Dropping mercury electrode	(a) Expanding plane (linear diffusion) (b) Expanding sphere (spherical diffusion)
Stirred solutions	Convection-limited diffusion
Solid planar electrode	Diffusion-layer model
Rotating disc electrode	Laminar flow model
Thin layer cells	Bounded diffusion

1.3.2. The Different Approaches in the Application of Combined A.C. and D.C. Perturbations

As can be seen in Section 1.2, there may be a certain dualism in the way to apply the a.c. perturbation: either one can prescribe the a.c. potential to be purely sinusoidal (a.c. potential control) leading to higher order (harmonics) terms in the a.c. current; or the reverse, the a.c. current is single-harmonic, leading to higher order terms in the potential response (a.c. current control).

Both alternatives could be combined with two analogous choices for the d.c. variable, i.e., d.c. current control and d.c. potential control.⁽⁴⁾ In view of the very scarce examples of the former in the literature,^(5,6) we will restrict this chapter to d.c. potential control.

It is not amazing that the a.c. potential control approach has been given considerable attention by those who were primarily interested in a.c. polarography. So there are detailed theories for several models: stationary plane,⁽⁷⁾ expanding plane,⁽⁸⁾ and stationary sphere.^(9,10) In these theories, the integral equations like Eq. (14) are substituted in the rate equation to eliminate the surface concentrations. Then the current density is solved via a series expansion analogous to Eq. (9), which directly gives all harmonics. For a detailed description of this derivation, the reader is referred to reference (7).

In the other approach (a.c. current control) advantage is taken of the fact that the a.c. components $\Delta c(0, t)$ of the surface concentrations can be solved directly from the integral equations after substitution of

$$j_F = j'_F + \Delta j_F = j'_F + j_{F,m} \sin \omega t \quad (15)$$

so that

$$c(0, t) = c'(0, t) + \Delta c(0, t) = c'(0, t) + a j_{F,m} \sin(\omega t - \theta) \quad (16)$$

However, a straightforward Taylor expansion of the rate equation analogous to Eq. (7) is hardly feasible because Eq. (10) cannot be inverted to an explicit expression for E . Therefore first the current is expanded in terms of Δc_i and ΔE , quite generally:^(11,12)

$$\begin{aligned} \Delta j_F = & \sum (\partial j_F / \partial c_i) \Delta c_i + (\partial j_F / \partial E) \Delta E + \frac{1}{2} \sum (\partial^2 j_F / \partial c_i^2) \Delta c_i^2 + \frac{1}{2} (\partial^2 j_F / \partial E^2) \Delta E^2 \\ & + \sum_{j \neq i} (\partial^2 j_F / \partial c_i \partial c_j) \Delta c_i \Delta c_j + \sum (\partial^2 j_F / \partial c_i \partial E) \Delta c_i \Delta E + \text{higher order terms} \end{aligned} \quad (17)$$

from which ΔE can be solved:

$$\begin{aligned} -\Delta E = & \frac{1}{\partial j_F / \partial E} [\sum (\partial j_F / \partial c_i) \Delta c_i - \Delta j_F] \\ & + \frac{1}{\partial j_F / \partial E} \left[\frac{1}{2} \sum (\partial^2 j_F / \partial c_i^2) \Delta c_i^2 + \sum_{j \neq i} (\partial^2 j_F / \partial c_i \partial c_j) \Delta c_i \Delta c_j \right] \end{aligned}$$

$$\begin{aligned}
& + \frac{1}{2} \frac{\partial^2 j_F / \partial E^2}{(\partial j_F / \partial E)^2} [\sum (\partial j_F / \partial c_i) \Delta c_i - \Delta j_F]^2 \\
& + \frac{\sum (\partial^2 j_F / \partial c_i \partial E) \Delta c_i}{\partial j_F / \partial E} [\sum (\partial j_F / \partial c_i) \Delta c_i - \Delta j_F] + \text{higher order terms.}
\end{aligned} \tag{18}$$

1.3.3. The Faradaic Impedance

On the basis of Eqs. (15) and (16) it can be seen that the first-order terms in Eqs. (17) and (18) represent the linear part of the faradaic response. The corresponding impedance can be found by introducing Eq. (15) and the relations between Δc_i and $j_{F,m}$ (Eq. (16)) and working out an expression like Eq. (3). However, especially in complex situations, this procedure is better bypassed by means of the operational definition of the faradaic impedance following Eq. (6):

$$Z_F = \frac{1}{\partial j_F / \partial E} \left\{ 1 - \sum_1^N (\partial j_F / \partial c_i) \frac{\overline{\Delta c_i(i\omega)}}{\Delta j_F(i\omega)} \right\} \tag{19}$$

and with Eq. (13)

$$Z_F = \frac{1}{\partial j_F / \partial E} \left\{ 1 - \sum_1^N (\partial j_F / \partial c_i) f_i(i\omega) \right\} \tag{20}$$

1.3.4. Double Layer Charging and Ohmic Drop

Like the faradaic process, charging of the electrical double layer is a non-linear process. The basic equations are most easily derived in terms of the relation between charge density q and potential. So, for a.c. potential control we have

$$\begin{aligned}
\Delta q &= \frac{dq}{dE} \Delta E + \frac{1}{2} \frac{d^2 q}{dE^2} \Delta E^2 + \dots \\
&= C_d \Delta E + \frac{1}{2} \frac{dC_d}{dE} \Delta E^2 + \dots
\end{aligned} \tag{21}$$

where C_d is the differential double layer capacity. For a.c. current control the expansion of E gives

$$\Delta E = \frac{1}{C_d} \Delta q - \frac{1}{2} \frac{1}{C_d^3} \frac{dC_d}{dE} \Delta q^2 + \dots \tag{22}$$

In both cases the charging current density is simply

$$\Delta j_C = \frac{d\Delta q}{dt} \tag{23}$$

Finally, the only linear process in the electrochemical cell is the conductance of electricity in the bulk of the solution and the leads towards the electrodes. This means that any current I passing the electrodes causes an ohmic drop $I \times R_\Omega$, which should be added to the interfacial potential ΔE , in order to obtain the electrode potential.

1.4. The Question of Steady State Behavior

Without special precautions, the start of the perturbation (at $t = 0$) occurs at an arbitrary moment within a period of the sine wave. This can be expressed, for instance in the a.c. current control case, by

$$\Delta I = I_m \sin(\omega t + \varepsilon) \quad (24)$$

When the object contains one or more delaying elements, the response will not immediately obtain its "proper" value, i.e., the value corresponding to Eq. (3). In fact the response of any object showing relaxation contains a "transient" term as is shown in Appendix I.

As an example, the voltage response of a parallel RC -circuit to a sinusoidal perturbation cf Eq. (24), starting at $t = 0$, is given by:

$$\begin{aligned} \Delta V = i_m \frac{1/R}{(1/R^2) + \omega^2 C^2} \sin(\omega t + \varepsilon) - \frac{\omega C}{(1/R^2) + \omega^2 C^2} \cos(\omega t + \varepsilon) \\ - i_m \left[\frac{1/R}{(1/R^2) + \omega^2 C^2} \sin(\varepsilon) - \frac{\omega C}{(1/R^2) + \omega^2 C^2} \cos(\varepsilon) \right] \exp(-t/RC) \end{aligned} \quad (25)$$

or, more generally, with $\cot \phi = 1/\omega RC$

$$\Delta V = i_m |Z| \sin(\omega t + \varepsilon - \phi) - i_m |Z| \sin(\varepsilon - \phi) \exp(-\omega t \cot \phi) \quad (26)$$

The time dependence of ΔV is shown in Figure 1.

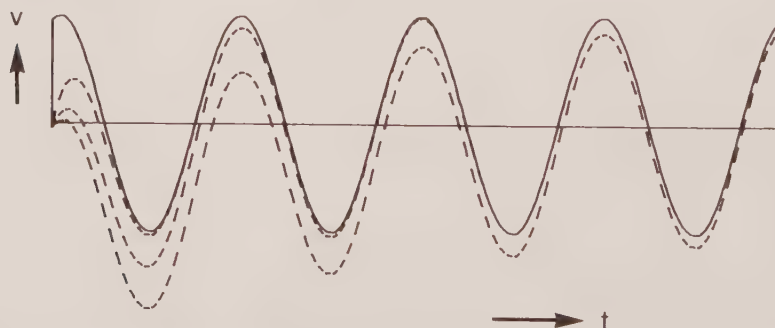


Figure 1. Transient voltage response of a parallel RC circuit. Solid line: $C = 0$; dashed lines: $\omega RC = 1, 3$ and 10 (upper to lower).

It can be concluded that the formal impedance concept can only be applied after a certain time when the transients have vanished. Steady state behavior is therefore defined as the situation where the output response is purely periodic. This is relevant also for faradaic processes, since changes in surface concentration due to a.c. electrolysis also contain transient terms (see Appendix I).

1.5. The Use of A.C. Methods in Electrochemistry

1.5.1. Historical

Application of alternating currents was proposed as early as 1868 by Kohlrausch to measure electrical conductances of electrolytes. The argument was that at sufficiently high frequencies "polarization" of the electrodes caused by the products of electrochemical reactions could be avoided.

This concentration polarization itself was the subject of interest in the famous studies of Warburg,⁽¹³⁾ intending to verify Fick's laws of diffusion in the case of silver ion reduction at silver electrodes. Warburg's theories describing diffusional mass transport due to sine wave currents were generalized later by Rosebrugh and Miller⁽¹⁴⁾ to other forms of periodic currents and also to aperiodic signals. Theoretical studies of this kind led to the concept of the "Warburg impedance" as the relation between a.c. voltage and current. However, it was not well understood that also the act of charge transfer at the interface could contribute to the electrode impedance, the charge transfer being assumed to proceed completely "reversibly."

In a separate field, impedance measurements have been applied for many years to obtain values of the differential double layer capacity at polarized electrodes [for a review see reference (15)]. It is remarkable to note that "double layer electrochemists" and the "kineticists" have been ignoring each other for such a long time, despite the close relations recognized nowadays. As regards methodology of a.c. electrolysis the link was made by Randles,⁽¹⁶⁾ by presenting his equivalent circuit, which combines the elements of charge transfer, diffusion, double layer capacitance, and electrolyte conductivity.

Although it is difficult to unravel the historical lines which led to a real new development, this work of Randles may be considered as the foundation of the now well-known impedance method for the investigation of electrode processes. However, the theory was restricted to a.c. perturbations of systems *initially at equilibrium*. The other important idea was that of Breyer, viz. to elaborate the *combined application of a.c. and d.c. polarization* with the aim of developing a new analytical technique called a.c. polarography.⁽¹⁷⁾ It is amazing that the theory for the latter remained unclear for more than ten years⁽⁸⁾ and that the potentialities for the study of electrode kinetics were recognized even later.^(18,19,20)

Similarly, the history of second-order techniques is almost confined to the last two decades. Although the rectifying and demodulating properties of electrochemical cells were observed experimentally already about 1900,⁽²¹⁾ the second-order phenomena were rediscovered as the faradaic rectification technique,^(11,22) second harmonic a.c. polarography,^(20,23,24) and the less popular demodulation and intermodulation polarography.⁽²⁵⁾ Both theory and instrumentation for these techniques are still developing.

1.5.2. *Fields of Application*

Thus far, the use of a.c. techniques has been proved in three domains:

- the investigation of electrochemical "objects": batteries, corroding systems, solid electrolytes, etc. The aim is to describe the properties of the system in terms of impedance parameters, which can be interpreted in terms of physico-chemical phenomena;
- analytical chemistry: the a.c. polarographic performance with modern instrumentation offers a sensitive analysis technique, comparable with differential pulse polarography. Although the latter is nowadays far more popular, it is sure that a.c. polarography might be of more help in the case of complex systems, because as yet, it is theoretically better understood;
- the extension of the science of thermodynamics and kinetics at and in the vicinity of (electrode) interfaces; more concretely, the design of models to describe a system and the comparison of this model with experimental facts.

1.5.3. *Place among the Relaxation Techniques*

One may question in what aspects the steady state a.c. methods are distinct from the numerous existing so-called transient relaxation methods. It is beyond our scope to deal with the answer extensively, but we like to extract some points of view from two interesting papers by Reinmuth⁽²⁶⁾ and Rangarajan.⁽²⁷⁾

- From an historical point of view it can be said that the transient methods have been confined to the most elementary "Randles model", whereas in the meantime more complex equivalent circuits for more complex situations (e.g., coupled chemical reactions, reactant adsorption) have been designed and verified by impedance measurements.
- However, this difference is trivial since in Laplace transformed state the characteristics for transients are equally simple (or complex) as the impedance expressions. Therefore, the content for information of a transient response in a certain time domain must be equivalent to that of an impedance measured in the corresponding frequency domain. One could conclude that experimentally the measurement of one transient is preferable to the measurement of a number of impedances at different frequencies.

- However, though some transient methods offer elegant possibilities to eliminate unwanted complications (e.g., double layer charging in the galvanostatic double pulse method), the transient method is always based on the assumption of a certain model, and its confirmation requires verification of the whole transient behavior, thus involving the complicated theory.
- Moreover, the condition of linearity places many more constraints upon the transient method, because it is not possible to “filter” the higher order responses, as opposed to a.c. measurements.
- On the other hand, the very possibility offered by sine wave perturbation to obtain higher order responses separately is of fundamental importance: besides the fact that double layer charging is less dominant, Reinmuth has shown that only combined examination of first-order and second-order data provides the kinetic parameters necessary to determine the mechanism of charge transfer unambiguously.

2. The Randles Equivalent Circuit

2.1. Introduction

At present, the qualification “Randles circuit” is used to indicate that the system behaves in accordance with the most simple boundary conditions postulated by Randles, distinct from the more complex situations, which were considered later. The main subject of this section is this “Randles behavior”, but in addition we will point to the complications or limitations imposed by the experimental conditions described in Table 1. Different behavior due to “chemical” complications will be treated in section 5.

2.2. Premises

(i) The object of the experiment is supposed to be an electrochemical cell containing a sufficient amount of supporting electrolyte and one or both of the components involved in a (pseudo)–first-order electrode reaction with simultaneous electron transfer:



The rate equation, formulated in Eq. (10), reads in this case:

$$\begin{aligned} -j_F &= nF[k_f C_O(0, t) - k_b C_R(0, t)] \\ &= nFk_f [C_O(0, t) - C_R(0, t) \exp \varphi] \end{aligned} \quad (27)$$

with $\varphi = (nF/RT)(E - E^\circ)$

(ii) The species *Ox* and *Red* are not involved in rate-determining chemical reactions.

(iii) The species *Ox* and *Red* are not involved in other interfacial processes such as (specific) adsorption, surface diffusion, or crystallization.

The equivalent circuit for the impedance of the working electrode of this system is shown in Figure 2.

2.3. The Faradaic Impedance

Application of the first-order expansion in Eq. 18 to Eq. 27 leads to

$$\frac{nF}{RT} \Delta E = \frac{\Delta j_F / nFk_F + \Delta c_O - \Delta c_R \exp \varphi}{\alpha c'_O + (1 - \alpha) c'_R \exp \varphi} \quad (28)$$

where c'_O and c'_R are the mean concentrations at the electrode surface, imposed by d.c. polarization. According to Eq. (20) the faradaic impedance is given by

$$Z_F = \frac{RT}{nF} \frac{1/nFk_F + f_O(i\omega) - f_R(i\omega) \exp \varphi}{\alpha c'_O + (1 - \alpha) c'_R \exp \varphi} \quad (29)$$

The diffusional part of Z_F can be elaborated by specification of $f_O(i\omega)$ and $f_R(i\omega)$ [(cf. Eq. (13)], in relation to the models of Table 1 and the corresponding solutions of the diffusion problem in Laplace notation.

2.3.1. Semi-infinite Linear Diffusion

The necessary requirement to solve the a.c. diffusion problem is that the electrolysis time is large as compared to the reciprocal of frequency: $t \gg 1/\omega$,⁽²⁸⁾ see Appendix I. With this condition, it can be shown^(29,8,30) that the solutions for the *stationary planar electrode* and the *expanding planar electrode* are identical. The solution is (see Appendix II)

$$f_{O,R}(i\omega) = \pm \frac{1}{nF(i\omega D_{O,R})^{1/2}} \quad (30)$$

where the plus sign pertains to *Ox*, the minus sign to *Red*. This leads to

$$Z_F = R_{ct} + (\sigma_O + \sigma_R) \omega^{-1/2} (1 - i) \quad (31)$$

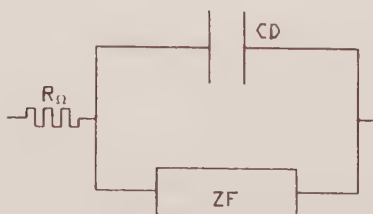


Figure 2. Randles equivalent circuit.

with

$$R_{ct} = \frac{RT}{n^2 F^2 k_f} \frac{1}{\alpha c'_O + (1 - \alpha) c'_R \exp \varphi} \quad (32)$$

$$\sigma_O = \frac{RT}{n^2 F^2 2^{1/2}} \frac{D_O^{-1/2}}{\alpha c'_O + (1 - \alpha) c'_R \exp \varphi} \quad (33a)$$

$$\sigma_R = \frac{RT}{n^2 F^2 2^{1/2}} \frac{D_R^{-1/2} \exp(\varphi)}{\alpha c'_O + (1 - \alpha) c'_R \exp \varphi} \quad (33b)$$

Equation 31, representing the faradaic impedance as the sum of the *charge transfer resistance* R_{ct} and the *Warburg impedance* $(\sigma_O + \sigma_R)\omega^{-1/2}(1 - i)$, is the essential expression for what we call "Randles behavior", symbolized by the equivalent circuit of Figure 3a.

2.3.2. Semi-infinite Spherical Diffusion

At spherical electrodes Randles behavior will be disturbed at lower frequencies due to the different equivalent circuit,⁽³¹⁾ cf. Figure 3b. The spherosymmetrical diffusion problem is easily solved in Laplace form⁽³⁾ and leads to the following expression for the faradaic impedance (see Appendix II):

$$Z_F = R_{ct} + \sum_{O,R} \sigma_{O,R} \omega^{-1/2} \frac{1 + y_{O,R} - i}{1 + y_{O,R} + (1/2)y_{O,R}^2} \quad (34)$$

where

$$y_{O,R} = \pm(2D_{O,R}/\omega)^{1/2} r_0^{-1}$$

The minus sign holds for species soluble in the electrode phase.

2.3.3. Bounded or Limited Diffusion

Replacement of the boundary condition $\Delta c(\infty, t) = 0$ by $\Delta C(\delta, t) = 0$ also leads to a more complex character of the diffusional impedance in the lower

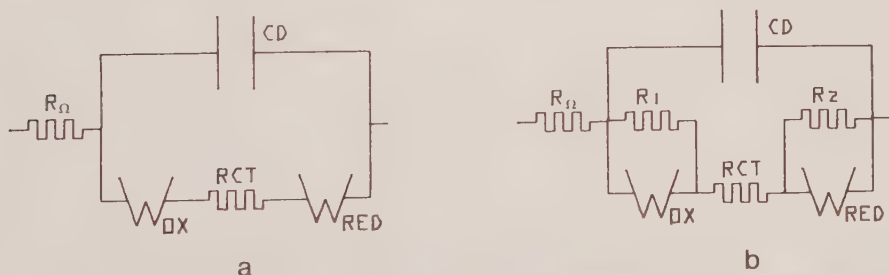


Figure 3. Equivalent circuit for (a) semi-infinite linear diffusion, (b) semi-infinite spherical diffusion.

frequency region.⁽³²⁾

$$Z_F = R_{ct} + \sum_{O,R} \sigma_{O,R} \omega^{-1/2} \frac{\text{sh}(2\mu_{O,R})(1-i) + \sin(2\mu_{O,R})(1+i)}{\text{ch}(2\mu_{O,R}) + \cos(2\mu_{O,R})} \quad (35)$$

where

$$\mu_{O,R} = \delta_{O,R}(\omega/2D_{O,R})^{1/2} \quad (36)$$

See Appendix II.

2.4. Frequency Dependence and Complex Plane Representation

Evidently the essential variable in Eqs. (31) to (36) describing the faradaic impedance is $\omega^{-1/2}$. Figure 4 shows characteristic plots of Z'_F and Z''_F against $\omega^{-1/2}$ for the three cases of Section 2.3 (Randles' plots).

A drawback of such plots is that they cannot visualize the behavior approached at zero frequency. Therefore it is convenient also to consider the complex plane representation of $Z_F = Z'_F - iZ''_F$ (i.e., Z''_F plotted against Z'_F for varying frequency). This is done in Figure 5 for the case of bounded diffusion. The real impedance obtained at zero frequency is equal to the so-called polarization resistance, i.e., the derivative of the $E-j_F$ characteristic for direct current.

The frequency at which the influence of electrode curvature becomes negligible is different for the real component Z'_F and the imaginary component

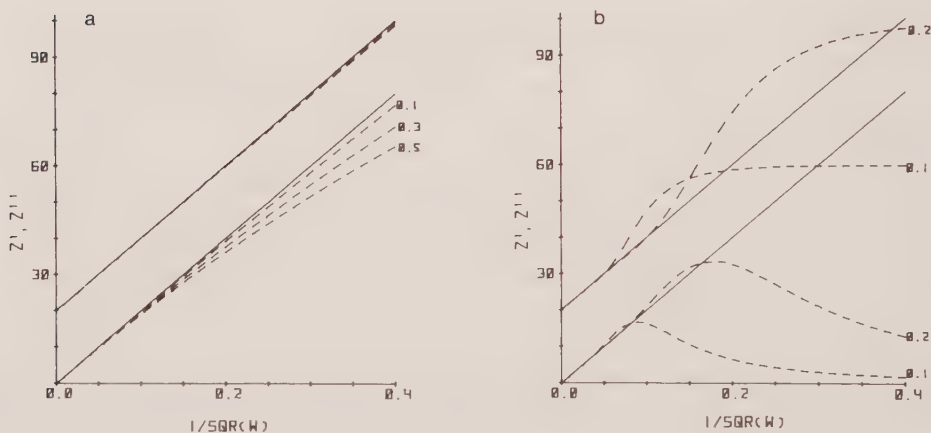


Figure 4. Randles' plots of the faradaic impedance for $R_{ct} = 20 \Omega \text{ cm}^2$, $\sigma_O = \sigma_R = 100 \Omega \text{ cm}^2 \text{ s}^{-1/2}$. Upper set of curves: Z'_F ; lower set: Z''_F . Solid lines: Warburg impedance. Dashed curves: (a) spherical diffusion; values of $(2D_{O,R})^{1/2}/r_0$ indicated, (b) bounded or limited diffusion; values of $\delta(2D_{O,R})^{-1/2}$ indicated.

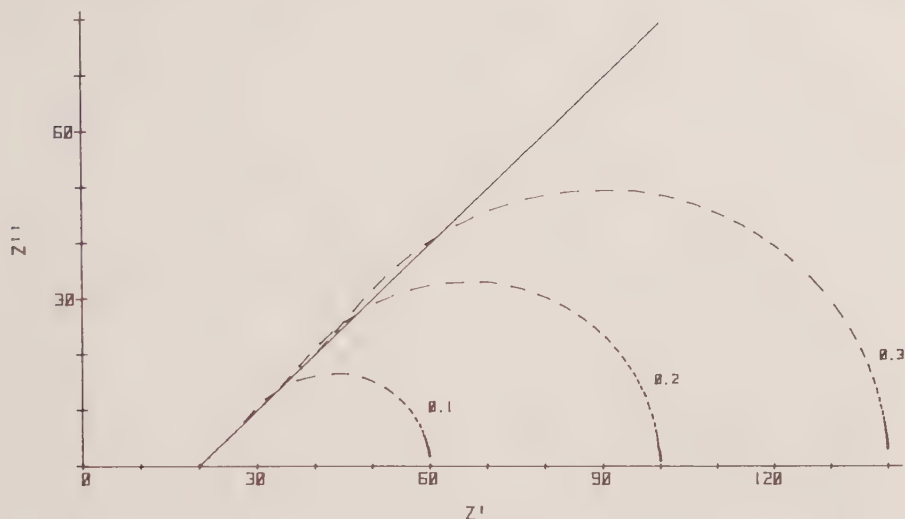


Figure 5. Complex plane representation of Figure 4b. Solid line: Randles behavior.

Z''_F . In Table 2 the correction factors of Eq. (34) are given for radius values 2×10^{-2} cm and 5×10^{-2} cm and a diffusion coefficient of 10^{-5} cm² s⁻¹. Similarly, the correction factors for Eq. (35) are given for several thicknesses of the diffusion layer.

The conclusion is that in usual cases with unstirred solutions Randles behavior can be expected at frequencies above 10 Hz.

Naturally the frequency dependence of the entire Randles circuit is complicated by the presence of the double layer capacitance C_d . It may be noted that normally the value of C_d is assumed equal to its value measured in the absence of the electro-active species at the same d.c. potential. Again, the complex plane representation is most useful to visualize the frequency dependence (Figure 6). Detailed discussions presented previously⁽³³⁾ can be summarized as follows:

(a) The *general expression* for Z is

$$Z = R_\Omega + \frac{R_{ct} + \sigma\omega^{-1/2} - i[\omega C_d(R_{ct} + \sigma\omega^{-1/2})^2 + \sigma^2 C_d + \sigma\omega^{-1/2}]}{(\sigma\omega^{1/2} C_d + 1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma\omega^{-1/2})^2} \quad (37)$$

with

$$\sigma = \sigma_O + \sigma_R \quad (38)$$

(b) *High-frequency behavior*: provided that $\sigma\omega^{1/2} C_d$ is sufficiently small, and $R_{ct} \gg \sigma\omega^{-1/2}$, terms in σ disappear from Eq. (37) at high frequencies.

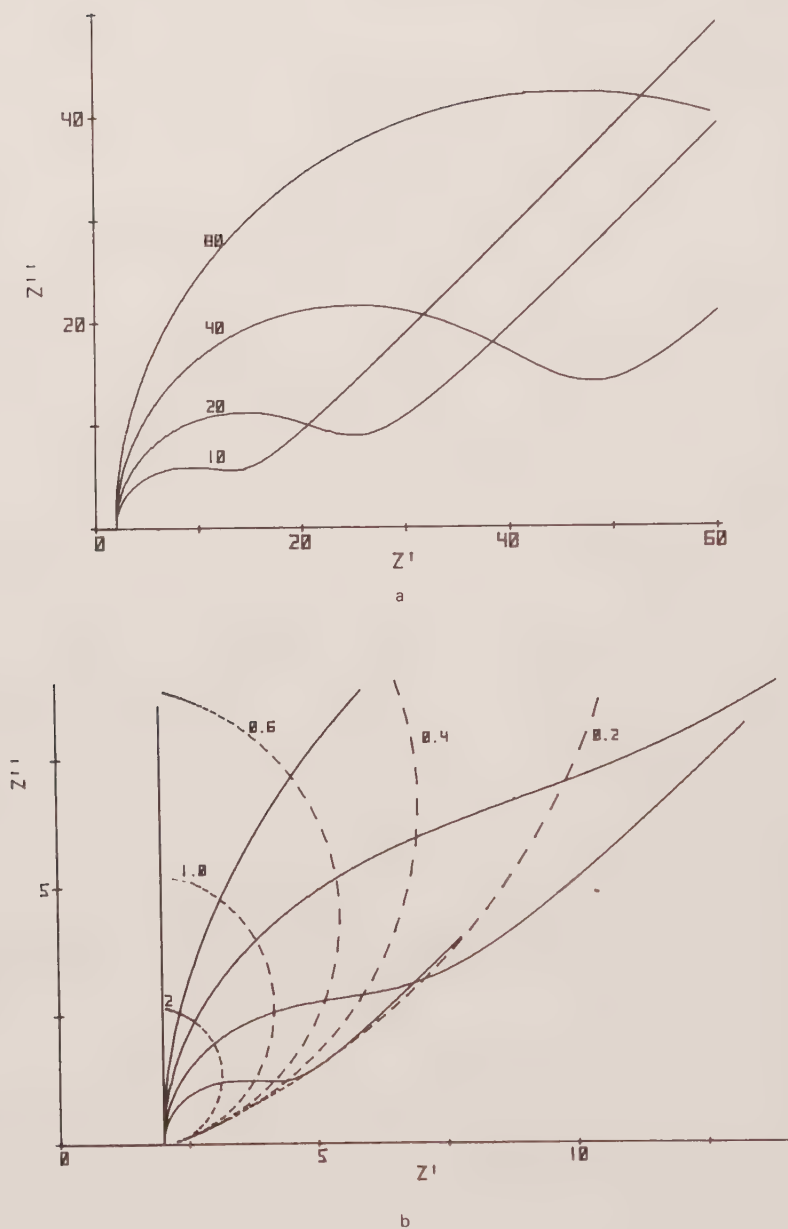


Figure 6. (a) Complex plane plots for frequency variation. $C_d = 30 \mu\text{F cm}^{-2}$, $R_\Omega = 2 \Omega \text{ cm}^2$, $\sigma_O = \sigma_R = 40 \Omega \text{ cm}^2 \text{ s}^{-1/2}$, R_{ct} indicated (in $\Omega \text{ cm}^2$) at different curves. (b) Complex plane plots for frequency variation (solid curves). $C_d = 30 \mu\text{F cm}^{-2}$, $R_\Omega = 2 \Omega \text{ cm}^2$; from left to right: $R_{ct} = \infty$, 16, 8, 4, 2 $\Omega \text{ cm}^2$, $\sigma_O = \sigma_R = 10 R_{ct} \Omega \text{ cm}^2 \text{ s}^{-1/2}$. The dashed curves connect points of equal frequencies, indicated in KHz.

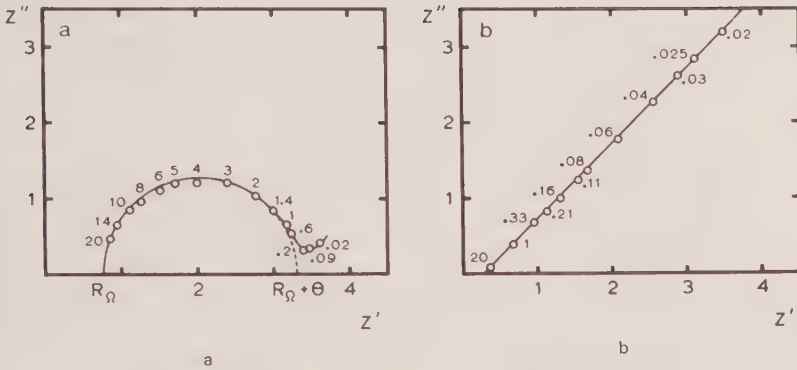


Figure 7. Complex plane plots for frequency variation of (a) a hanging Zn amalgam drop electrode in 1 M NaClO₄ + 10⁻³ M HClO₄. $C_{Zn^{2+}} = c_{Zn(Hg)} = 8 \cdot 10^{-6}$ moles cm⁻³; (b) a hanging mercury drop electrode in 1 M HClO₄ + 2.10⁻⁶ moles cm⁻³ Hg₂²⁺. Numbers indicate frequency in KHz.⁽³⁴⁾

Then a semi-circle appears in the complex plane plot. Intersection with the Z' axis occurs at $Z' = R_{\Omega}$ and at $Z' = R_{\Omega} + R_{cr}$.

(c) *Low-frequency behavior*: omission of higher powers of $\omega^{1/2}$ leads to a plot similar to Figure 2.4, suggesting that the double layer capacitance has no influence. However, the intersection with the Z' axis occurs at $Z' = R_{\Omega} + R_{ct} - 2\sigma^2 C_d$ instead of $Z' = R_{\Omega} + R_{cr}$.

Experimental examples of high- and low-frequency behavior are shown in Figure 7. Complex plane plots of these types were introduced as a way to analyze measured impedances.⁽³⁴⁾ However, especially in frequently occurring intermediate cases, numerical procedures are preferable.⁽¹⁸⁾ Nevertheless, graphs like Figure 7 are useful for a first orientation, which may help to choose the analysis procedure (see section 2.6). In this respect, not only impedance plots, but also plots of the complex *electrode admittance* Y_{el} are useful.⁽³⁵⁾ When it is possible to subtract R_{Ω} from Z' , one has:

$$Y_{el} = \frac{Z' - R_{\Omega} + iZ''}{(Z' - R_{\Omega})^2 + (Z'')^2} = Y'_{el} + iY''_{el} \tag{39}$$

Examples of electrode admittance plots are shown in Figure 8.

2.5. Potential Dependence

Expressions for the d.c. potential dependence of the mean concentrations c'_O and c'_R in Eqs. (32) and (33) are more or less complex, in view of the formulation of the d.c. mass transfer process and the influence of the charge transfer process (reversible or not reversible). Consequently the potential dependence of Z_F may be different for different models.

Table 2
Factors Expressing Influence of Curvature and of Limited
Diffusion Layer on the Mass Transport Impedance, of Eqs.
(34) and (35)

$(2D)^{1/2}/r_0 = 0.1 \text{ s}^{1/2}$				
Frequency Hz	Diff. in solution		Diff. in electrode	
	Real	Imag.	Real	Imag.
0.1	0.9930	0.8817	1.1340	0.9910
0.3	0.9975	0.9298	1.0755	0.9971
1	0.9992	0.9609	1.0407	0.9992
3	0.9997	0.9772	1.0233	0.9997
10	0.9999	0.9850	1.0127	0.9999
30	1.0000	0.9944	1.0048	1.0000
100	1.0000	0.9960	1.0040	1.0000

$(2D)^{1/2}/r_0 = 0.2 \text{ s}^{-1/2}$				
Frequency Hz	Diff. in solution		Diff. in electrode	
	Real	Imag.	Real	Imag.
0.1	0.9752	0.7787	1.2828	0.9592
0.3	0.9908	0.8648	1.1562	0.9877
1	0.9971	0.9234	1.0830	0.9966
3	0.9990	0.9550	1.0471	0.9989
10	0.9997	0.9751	1.0255	0.9997
30	0.9999	0.9855	1.0147	0.9999
100	1.0000	0.9921	1.0080	1.0000

Frequency Hz	$\delta/(2D)^{1/2} = 1^a$		$\delta/(2D)^{1/2} = 0.3$		$\delta/(2D)^{1/2} = 0.1$	
	Real	Imag.	Real	Imag.	Real	Imag.
0.1	0.7339	0.3105	0.2363	0.0807	0.0792	0.0265
0.3	1.0630	0.6170	0.4040	0.1447	0.1370	0.0461
1	1.1070	1.0042	0.7020	0.2909	0.2489	0.0853
3	0.9922	1.0166	1.0369	0.5794	0.4249	0.1534
10	1.0004	0.9997	1.1210	0.9848	0.7339	0.3105
30	1.0000	1.0000	0.9950	1.0222	1.0630	0.6170
100	1.0000	1.0000	1.0003	0.9993	1.1070	1.0042
300	1.0000	1.0000	1.0000	1.0000	0.9922	1.0166

^a Typical for DME

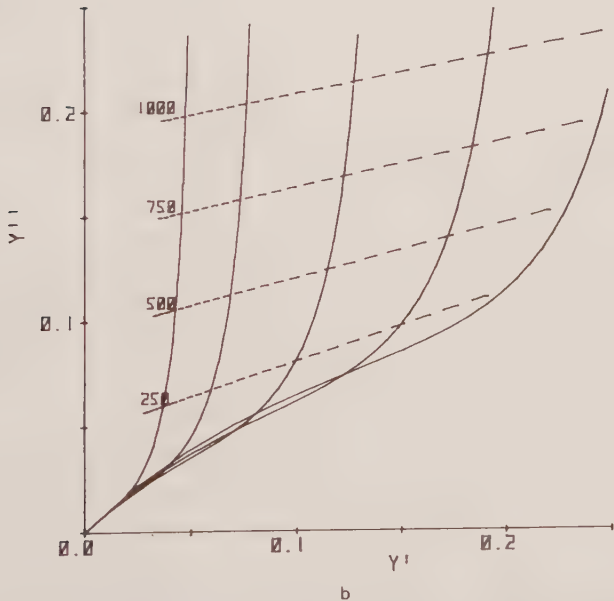
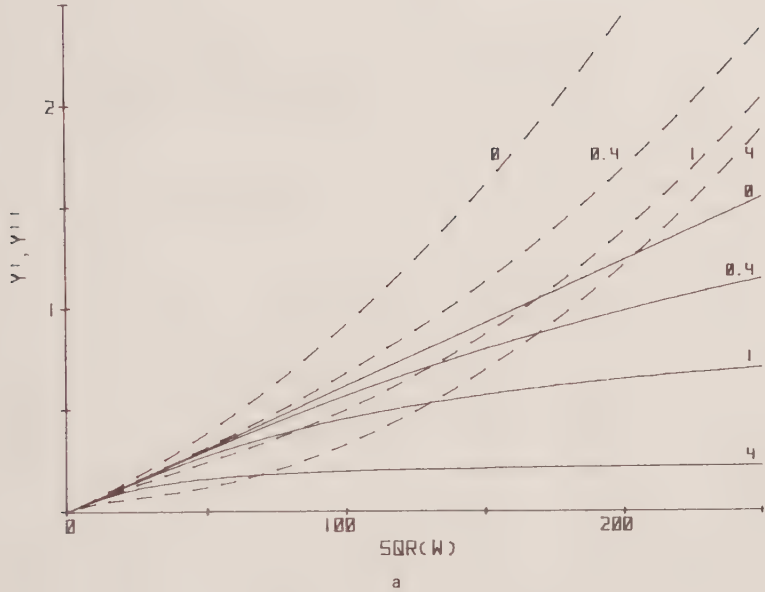


Figure 8. (a) Admittance components for Randles behavior as a function of frequency. Solid curves: Y'_{el} , dashed curves: Y''_{el} . $C_d = 30 \mu\text{F cm}^{-2}$, $\sigma_O = \sigma_R = 40 \Omega\text{ cm}^2\text{ s}^{-1/2}$. Different values of R_{ct} ($\Omega\text{ cm}^2$) as indicated. (b) Complex plane locus of electrode admittance for variation of frequency (solid curves), from left to right: $R_{ct} = 16, 10, 6, 4, 3 \Omega\text{ cm}^2$, $\sigma_O = \sigma_R = 10R_{ct}$, $C_d = 30 \mu\text{F cm}^{-2}$. The dashed straight lines connect points of equal frequency, indicated in Hz.

2.5.1. "Rigorous" Models

The most simple expressions are found to be valid for a *d.c. reversible* system with semi-infinite diffusion towards a *planar* electrode (stationary or expanding):

$$c'_O D_O^{1/2} = c'_R D_R^{1/2} e^\zeta = (c_O^* D_O^{1/2} + c_R^* D_R^{1/2}) \frac{e^\zeta}{1 + e^\zeta} \quad (40)$$

with

$$\begin{aligned} \zeta &= (nF/RT)(E - E'_{1/2}) \\ &= (nF/RT)(E - E^\circ) + \ln(D_O/D_R)^{1/2} \end{aligned} \quad (41)$$

N.B. The use of ζ (potential referred to the *reversible* half-wave potential) leads to the most convenient notations and is therefore frequently applied in literature. When desired, a notation in terms of $\exp \varphi$ is, of course, easily derived.

For systems complicated by irreversibility and/or sphericity the appropriate *d.c.* theory leads to "corrected" expressions, which can be written in a general form:

$$c'_O D_O^{1/2} = (c_O^* D_O^{1/2} + c_R^* D_R^{1/2}) \frac{e^\zeta}{1 + e^\zeta} + \frac{c_O^* D_O^{1/2} - c_R^* D_R^{1/2} e^\zeta}{1 + e^\zeta} H(t) \quad (42a)$$

$$c'_R D_R^{1/2} = (c_O^* D_O^{1/2} + c_R^* D_R^{1/2}) \frac{1}{1 + e^\zeta} + \frac{c_O^* D_O^{1/2} - c_R^* D_R^{1/2} e^\zeta}{1 + e^\zeta} H'(t) \quad (42b)$$

where the functions $H(t)$ and $H'(t)$ (always closely related) are defined by the specific problem.

From Eqs. (31) to (36) and (40) to (42) it follows that the potential dependence of the faradaic impedance in the *d.c. reversible* case ("Nernstian behavior") is determined by the equations:⁽³³⁾

$$R_{ct,rev} = \frac{RT}{n^2 F^2} \frac{D_O^{1/2}}{c_O^* D_O^{1/2} + c_R^* D_R^{1/2}} \frac{1 + e^{-\zeta}}{k_f} \quad (43)$$

$$\sigma_{O,rev} = \sigma_{R,rev} e^{-\zeta} = \frac{RT}{n^2 F^2 2^{1/2}} \frac{1}{c_O^* D_O^{1/2} + c_R^* D_R^{1/2}} [1 + e^{-\zeta}] \quad (44)$$

while the complications introduced by "non-Nernstian behavior" are generally expressed by:^(30,33)

$$\frac{\sigma_O}{\sigma_{O,rev}} = \frac{\sigma_R}{\sigma_{R,rev}} = \frac{R_{ct}}{R_{ct,rev}} = \frac{1}{F(t)} \quad (45)$$

with

$$F(t) = 1 + \frac{c_O^* D_O^{1/2} - c_R^* D_R^{1/2} e^\zeta}{c_O^* D_O^{1/2} + c_R^* D_R^{1/2}} [\alpha e^{-\zeta} H(t) + (1 - \alpha) H'(t)] \quad (46)$$

Expressions for the time-dependent term in Eq. (46) are collected in Table 3. Note that naturally $F(t) = 1$ at the equilibrium potential: $\exp(\zeta_{eq}) = c_O^* D_O^{1/2} / c_R^* D_R^{1/2}$.

2.5.2 Diffusion Layer Models

The rather complex mathematics involved by the equations in the foregoing section may be avoided by using the well-known approximate solution of the integral equation (14):^(36,3)

$$c'(0, t) = c^* \pm \frac{j_F'}{nFD} \delta \quad (47)$$

where δ is constant for convection-limited diffusion (see Table 1), but a specific function of time in the cases mentioned in Table 3. Combining Eq. (47) and (27), it is easily verified that the function $F(t)$ becomes

$$F(t) = 1 + \frac{c_O^* D_O^{1/2} - c_R^* D_R^{1/2} e^\zeta}{c_O^* D_O^{1/2} + c_R^* D_R^{1/2}} \times \frac{[\alpha e^{-\zeta} - (1 - \alpha)] D_O^{1/2} / k_f + \delta_R / D_R^{1/2} - \delta_O / D_O^{1/2}}{(D_O^{1/2} / k_f) + (\delta_R / D_R^{1/2}) e^\zeta + (\delta_O / D_O^{1/2})} \quad (48)$$

Use of this equation has the advantage that general predictions are possible on the basis of analytical expressions instead of numerical calculations. Such predictions have been made in detail previously.⁽³³⁾ They are summarized in Table 4 and illustrated in Figures 9, 10, and 11.

2.5.3. The Faradaic Phase Angle

The relative contributions of R_{ct} and σ to the faradaic impedance are reflected in the faradaic phase angle ϕ , given by:

$$\cot \phi = Z_F' / Z_F'' = 1 + R_{ct} / \sigma \omega^{-1/2} = 1 + p \quad (49)$$

so with Eq. (38) and Eqs. (43) to (45)

$$p = \frac{(2D_O)^{1/2}}{k_f(1 + \exp \zeta)} \omega^{1/2} \quad (50)$$

Table 3

Model	$\alpha \exp(-\xi)H(t) + (1-\alpha)H'(t)$	Reference	δ
Stat. plane, irr $H'(t) = -H(t)$	$[\alpha \exp(-\xi) - (1-\alpha)] \exp(\lambda^2 t) \operatorname{erfc}(\lambda t^{1/2})$	(30)	$(\pi D)^{1/2}$
Exp. plane, irr $H'(t) = -H(t)$	$[\alpha \exp(-\xi) - (1-\alpha)] \left\{ 1 + \sum_{i=1}^{\infty} (-1)^i \prod_{j=1}^i B \left(\frac{3k+7}{14}, \frac{1}{2} \right) \left[\frac{(3t/7\pi)^{1/2-\lambda}}{1} \right]^i \right\}$ or approximated: a) $[\alpha \exp(-\xi) - (1-\alpha)] (7/3\pi)^{1/2} \frac{1.61 + \lambda t^{1/2}}{(1.13 + \lambda t^{1/2})^2}$ b) $[\alpha \exp(-\xi) - (1-\alpha)] (7/3\pi)^{1/2} / \lambda t^{1/2} [1 + (1.35 \lambda t^{1/2})^{-1.091}]$	(8) (7, 10) (8) (7, 10) (10)	$(3\pi D/7)^{1/2}$ $(\pi D)^{1/2} r_0 / [(\pi D)^{1/2} \pm r_0]$
Stat. sphere, rev $H'(t) = H(t) \exp(-\xi)$	$\frac{D_O^{1/2} \exp(\xi) \pm D_R^{1/2}}{D_O^{1/2} \exp(\xi) \pm D_R^{1/2}} [1 - \exp(a^2 t) \operatorname{erfc}(at^{1/2})]$, with $a = (\xi_O \exp(\xi) \pm \xi_R) / (\exp(\xi) + 1)$, upper sign: R soluble in solution phase, lower sign: R soluble in electrode phase. $[\alpha \exp(-\xi) - (1-\alpha)] \times \{ \xi_O \xi_R / (A+B)(A-B) + 1/2[\lambda/B - 1 + \xi_O \xi_R / (A-B)B] \exp(A-B)^2 t \operatorname{erfc}(A-B)t^{1/2} - 1/2[\lambda/B + 1 + \xi_O \xi_R / (A+B)B] \exp(A+B)^2 t \operatorname{erfc}(A+B)t^{1/2} + \lambda(\xi_O^- \xi_R) / (\exp \xi + 1) \times 1/(A+B)(A-B) - 1/2 B(A-B) \exp(A-B)^2 t \operatorname{erfc}(A-B)t^{1/2} + 1/2 B(A+B) \exp(A+B)^2 t \operatorname{erfc}(A-B)t^{1/2}$, with $A = \lambda + \xi_O + \xi_R$, $B^2 = A - 4 \left[\frac{\xi_O \exp(\xi) + \xi_R}{\exp(\xi) + 1} \right]$	(10)	$(\pi D)^{1/2} r_0 / [(\pi D)^{1/2} \pm r_0]$
R soluble in electrode Exp. sphere, rev Exp. sphere, irr	Identical, with ξ_R replaced by $-\xi_R$ See reference	(30)	$(3\pi D/7)^{1/2} r_0 / (3\pi D/7)^{1/2} \pm r_0]$

^a $\lambda = k_f (\exp(\xi) + 1) D_O^{-1/2}$, $\xi_O, \xi_R = D_O^{1/2}/r_O, D_R^{1/2}/r_O$

Table 4
Limiting Cases for the Faradaic Impedance

Behavior	Condition	Limiting case
Nernstian	$E = E_{1/2}$	$\sigma = \sigma_{\min} = \frac{4RT/2^{1/2}}{n^2 F^2 (c_O^* D_O^{1/2} + c_R^* D_R^{1/2})}$
	$E = E'_{1/2} + \frac{RT}{nF} \ln \frac{1-\alpha}{\alpha}$	$R_{ct} = R_{ct,\min}$
		$= \frac{RTD_O^{1/2}}{n^2 F^2 (c_O^* D_O^{1/2} + c_R^* D_R^{1/2}) k_f (1-\alpha)}$
	$E - E^\circ \rightarrow +\infty$	$\sigma \rightarrow (\sigma_m/4) \exp \zeta$
		$R_{ct} \rightarrow \frac{RTD_O^{1/2}}{n^2 F^2 (c_O^* D_O^{1/2} + c_R^* D_R^{1/2}) k_f} \frac{1}{\exp \zeta}$
D.C. irreversible	$E - E^\circ \rightarrow -\infty$	$\sigma \rightarrow (\sigma_m/4) \exp(-\zeta)$
		$R_{ct} \rightarrow \frac{RTD_O^{1/2}}{n^2 F^2 (c_O^* D_O^{1/2} + c_R^* D_R^{1/2})} \frac{\exp(-\zeta)}{k_f}$
	$E - E^\circ \gg 0$	
	a) $k_f \exp \varphi$ small	$R_{ct} = \frac{RT}{n^2 F^2 c_R^*} \frac{\delta_R/D_R + 1/(k_f \exp \varphi)}{1-\alpha}$
		$\sigma = \frac{RT}{n^2 F^2 c_R^* (2D_R)^{1/2}} \frac{\delta_R/D_R + 1/(k_f \exp \varphi)}{(1-\alpha)/(k_f \exp \varphi)}$
	b) $k_f \exp \varphi$ large ($E - E^\circ \rightarrow \infty$)	$R_{ct} = \frac{RT}{n^2 F^2 C_R^*} \frac{\delta_R}{(1-\alpha) D_R}$
		$\sigma = \frac{RT}{n^2 F^2 C_R^* (2D_R)^{1/2}} \frac{\delta_R k_f \exp \varphi}{(1-\alpha) D_R}$
	$E - E^\circ \ll 0$	
	c) k_f small	$R_{ct} = \frac{RT}{n^2 F^2 C_O^*} \frac{\delta_O/D_O + 1/k_f}{\alpha}$
		$\sigma = \frac{RT}{n^2 F^2 C_O^* (2D_O)^{1/2}} \frac{\delta_O/D_O + 1/k_f}{\alpha/k_f}$
	d) k_f large ($E - E^\circ \rightarrow \infty$)	$R_{ct} = \frac{RT}{n^2 F^2 c_O^*} \frac{\delta_O}{\alpha D_O}$
		$\sigma = \frac{RT}{n^2 F^2 c_O^* (2D_O)^{1/2}} \frac{\delta_O k_f}{\alpha D_O}$

Evidently, when $p > 10$, R_{ct} is the major part of Z_F , while for $p < 0.1$, the Warburg impedance dominates. It is important to notice that this expression for p holds for any model in Table 1 in the frequency region of Randles behavior. It is, therefore, a valuable diagnostic parameter.

2.5.4. The Faradaic Region

From Figures 9 to 11 it can be seen that Z_F must increase exponentially on either side of a minimum. The larger Z_F , the more it will be short-circuited

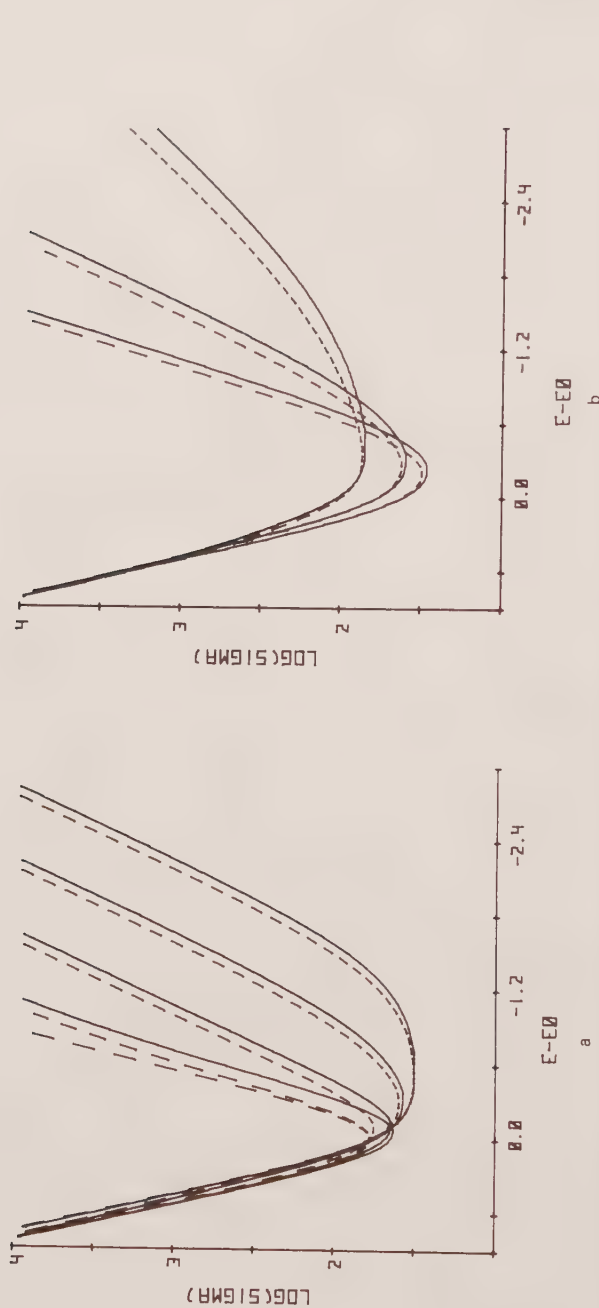


Figure 9. Potential dependence of the Warburg coefficient. Numerical data: $D_O = D_R = 10^{-5}$ cm² s⁻¹, $n = 2$, $c_O^* = 10^{-6}$ mole cm⁻³, $c_R^* = 0$, $k_f = k_{sh} \exp[-\alpha n F (E - E^0)/RT]$ with: (a) from left to right: $k_{sh} = 10^{-1}$, 10^{-2} , 10^{-3} , 10^{-4} , 10^{-5} cm s⁻¹; $\alpha = 0.5$; solid curves: spherical diffusion ($\tau_0/t^{1/2} = 0.01$), dashed curves: planar diffusion. (b) from left to right: $\alpha = 0.75$, 0.5 , 0.25 with $k_{sh} = 10^{-4}$ cm s⁻¹, planar diffusion; dashed curves: $t = 9$ s, solid curves: $t = 4$ s.

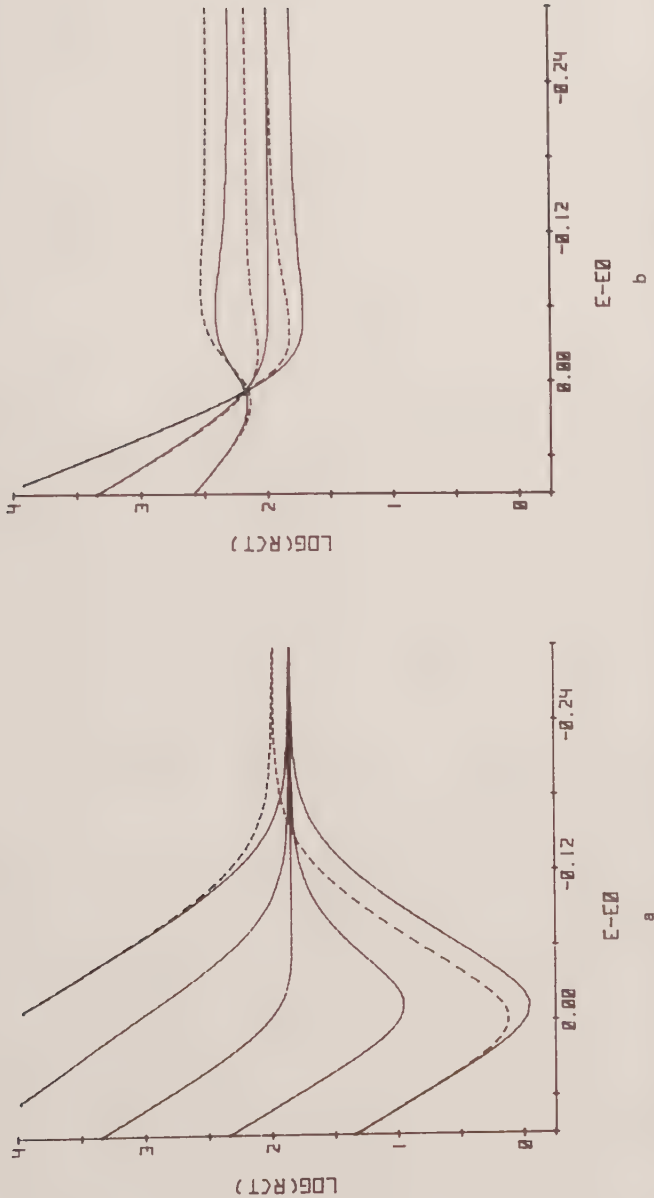
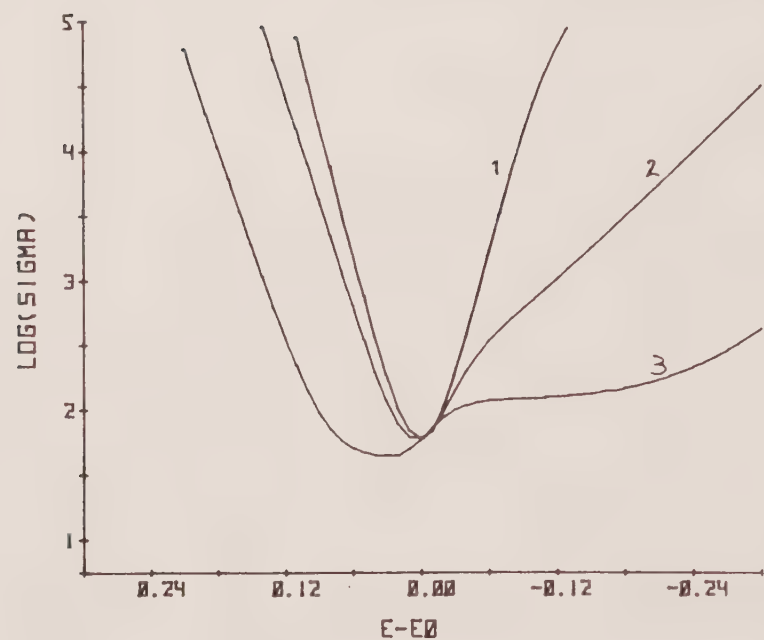
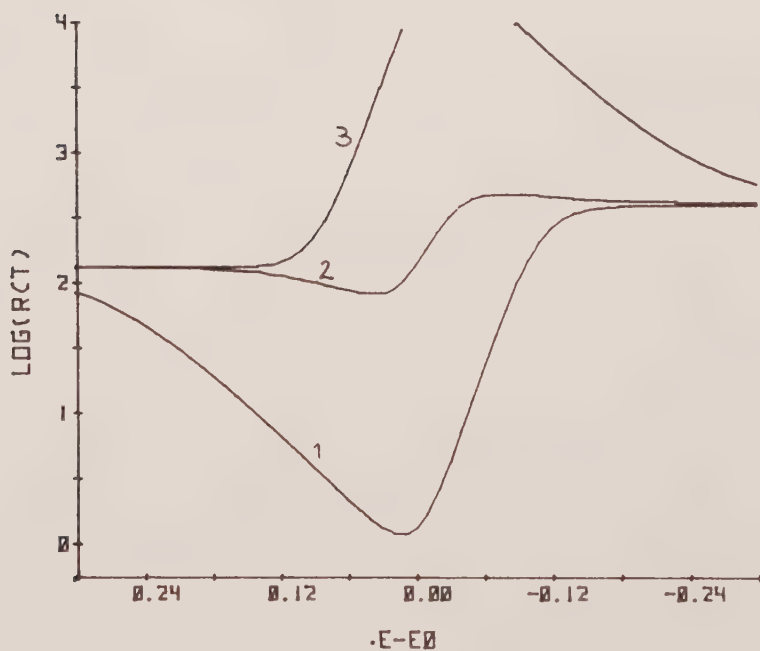


Figure 10. Potential dependence of the charge transfer resistance. Numerical data as in Figure 9, with: (a) from lower to upper curve: $k_{sh} = 10^{-1}$, 10^{-2} , 10^{-3} , 10^{-4} , 10^{-5} cm s $^{-1}$, $\alpha = 0.5$; dashed curves: planar diffusion, solid curves: spherical diffusion ($r_0/t^{1/2} = 0.01$). (b) from left to right: $\alpha = 0.25$, 0.5, 0.75 with $k_{sh} = 10^{-3}$ cm s $^{-1}$, planar diffusion; dashed curves; solid curves: $t = 4$ s.



a



b

Figure 11. (a) As Figure 9a, with $c_R^* = c_O^* = 10^{-6}$ mole cm^{-3} . (b) As (Figure 10a, with $c_R^* = c_O^* = 10^{-6}$ mole cm^{-3} , $\alpha = 0.75$, $k_{sh} = 0.1$ (curve 1), 10^{-3} (curve 2), and 10^{-5} (curve 3) cm s^{-1} .

by the double layer capacity (see Figure 6). The region where Z_F causes a substantial deviation from the impedance corresponding to R_Ω and C_d alone is called the faradaic region. It coincides with the region of the d.c. polarographic wave, but for d.c. irreversible reactions the maximum deviation may occur far remote from the half-wave potential.

2.5.5. The Kinetic Parameters

For d.c. reversible reactions only k_f can be obtained directly, either from R_{ct} or p , while $\sigma \neq f(k_f)$. Then α should be determined from $k_f = f(E)$. In the case of irreversible behavior, also α appears directly in the expressions for both R_{ct} and σ . In the extreme case α is even the only parameter in R_{ct} (see Table 4).

2.6. Data Analysis

In principle at a certain potential only two measurements of the complex impedance at two different frequencies are necessary to solve the values of the elements R_Ω , C_d , R_{ct} , and $\sigma = \sigma_O + \sigma_R$ from Eq. (37). However, to be sure that Randles behavior prevails, it is preferable to have data at more frequencies, in a range as wide as possible. Moreover, this allows a more precise separation of the frequently overlapping contributions. The following procedures can be applied.

(i) Usually it is possible to determine R_Ω separately, either in the supporting electrolyte alone, or at a potential where Z_F is infinite. In both cases $Z' = R_\Omega$. Then, Eq. (39) can be applied to any other measured data to yield the electrode admittance which is given by:

$$Y_{el} = Y'_{el} + iY''_{el} = \left\{ \frac{\omega^{1/2}}{\sigma} \frac{p+1}{p^2+2p+2} \right\} + i \left\{ \frac{\omega^{1/2}}{\sigma} \frac{1}{p^2+2p+2} + \omega C_d \right\} \quad (51)$$

- (a) Randles' procedure:⁽¹⁶⁾ in the supporting electrolyte alone ($\sigma = \infty$) C_d follows immediately from Y''_{el} , measured *at the desired potential*. After subtraction from Eq. (51), the resulting faradaic admittance Y_F is transformed to the faradaic impedance $Z_F = R_{ct} + \sigma\omega^{-1/2}(1-i)$, so that R_{ct} and σ are immediately known. In a plot like Figure 4, Randles behavior can be checked. Of course, deviations at low frequencies may indicate and provide information on influences of electrode curvature and/or bounded diffusion.
- (b) An alternative to this procedure^(18,33) is to determine Y_{el} at fixed potential, but *varying concentration*. Then, for any frequency:

$$Y''_{el} = Y'_{el}/(p+1) + \omega C_d \quad (52)$$

so that p and C_d can be calculated. The check on Randles behavior follows from consistency between different frequencies.

- (c) *Frequency variation method*:^(18,33) It can be preferable to make use of the fact that Y'_{el} is independent of C_d , which reduces the problem to a fitting on only two parameters, σ and $p' = p\omega^{-1/2}$. A first check on Randles behavior is the success of the fit, the second the consistency with Y''_{el} , which after introduction of σ and p' should yield a constant C_d value.

The amount of information on the three elements to be obtained from Y_{el} can be qualitatively deduced from Figure 12. It should be noted that the precision of Y_{el} decreases at higher ω , because of the subtraction of R_Ω , as is shown by the vertical bars.

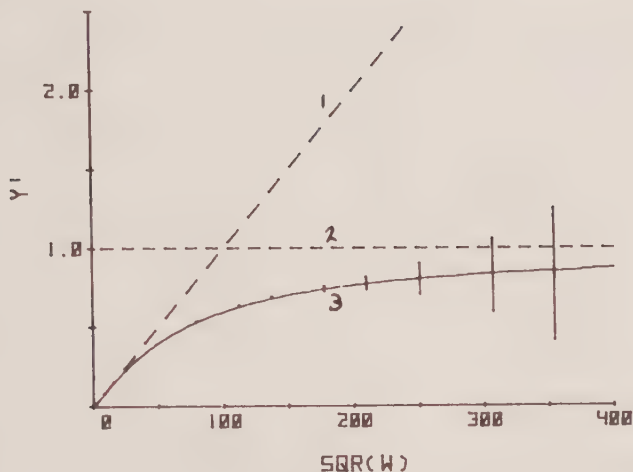
(ii) When it is not possible to determine R_Ω separately, a complete fitting analysis must be performed. Two approaches are conceivable:

- (a) *Extrapolation procedures*: in principle, extrapolation of Z' and Z'' , or any favorable function $Z'\omega^p$ and $Z''\omega^q$ to infinite frequency, yields values for R_Ω and C_d . However, these values may be contaminated by errors due to the influence of R_{ct} and σ on the actual data from which the extrapolation is performed. Therefore, after substitution of R_Ω and C_d at low frequencies, the resulting values of R_{ct} and σ must be inserted in the high-frequency data to check the consistency and, if necessary, to correct the extrapolated values. Sometimes many iterations will be required.
- (b) *Computerized fitting*: the general procedure is to compare the data with calculated ones from "trial values" for the elements, e.g., by a least squares minimization. The result is a set of values for R_Ω , C_d , σ , and R_{ct} which give the best fit *over the whole frequency range*. This procedure should be applied with great caution: Firstly, it is possible that deviations, although altogether at minimum, are systematic, which in fact proves inconsistency with Randles behavior. Secondly, the minimum may be relative, i.e., an (even lower) minimum exists for another set. Thirdly, artefacts may be introduced; for example, in a case like Figure 7b the computer will indicate a rather arbitrary set of values for R_Ω , R_{ct} , and C_d , since all the information on these parameters is contained in the intercept on the Z' -axis.

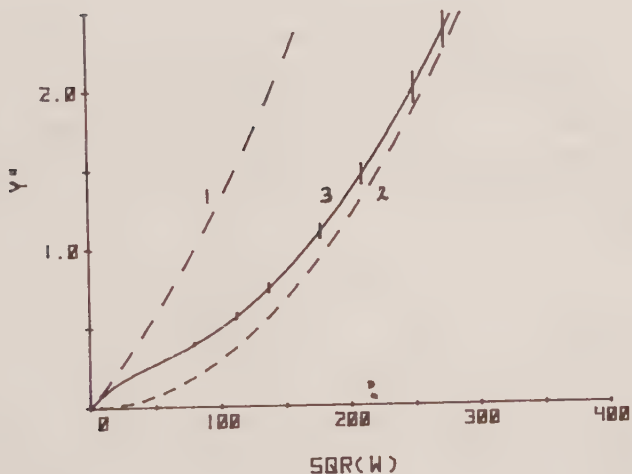
2.7. Choice of Variables (Input Parameters)

When it is intended to investigate the kinetics of the electrode process, it is useful to consider the amount of information that can be obtained. At fixed potential this depends on the choice of the remaining variables, concentration and frequency. Qualitatively, the following tendencies may be mentioned.

- (i) *At low concentration Z_F tends to infinity and the double layer admittance dominates. At high concentration Z_F tends to zero, thus short-circuiting the double layer admittance, but the ohmic resistance dominates.* From Figure 6 it can be seen that the most favorable concentration is such that $Z'' \approx 1/(2\omega C_d)$.



a



b

Figure 12. The contributions to the electrode admittance: (a) Y'_{el} , (b) Y''_{el} ; (1) $Y'_{el} = \omega^{1/2}/2\sigma$, $Y''_{el} = \omega^{1/2}/2\sigma + \omega C_d$; (2) $Y'_{el} = 1/R_{ct}$, $Y''_{el} = \omega C_d$; (3) $Y'_{el} = (R_{ct} + \sigma\omega^{-1/2})/[(R_{ct} + \sigma\omega^{-1/2})^2 + \sigma^2\omega^{-1}]$, $Y''_{el} = \sigma\omega^{-1/2}/[(R_{ct} + \sigma\omega^{-1/2})^2 + \sigma^2\omega^{-1}] + \omega C_d$. $\sigma = 50 \Omega \text{ cm}^2 \text{ s}^{-1/2}$, $R_{ct} = 1 \Omega \text{ cm}^2$, $C_d = 30 \mu\text{F cm}^{-2}$; vertical bars: uncertainty due to $0.01 \Omega \text{ cm}^2$ miscompensation in R_{Ω} .

(ii) At low frequency the double layer admittance tends to zero and Z_F dominates, with an increasing contribution of $\sigma\omega^{-1/2}$ relative to R_{ct} . The information on R_{ct} increases at higher frequencies, but at high frequencies the double layer admittance tends to short-circuit Z_F , so that the ohmic resistance dominates. Therefore, impedance measurements should be performed in a

frequency range as wide as possible, limited at the lower end by unwanted complications (mainly instrumental) and at the upper end by the time constant $R_{\Omega}C_d$.

More quantitatively, it can be put as follows. The amount of information concerning a parameter X is related to $\partial Z(i\omega)/\partial X$. The relative uncertainty in X is minimal when the function

$$\Delta_x = \frac{X}{Z' - iZ''} \left(\frac{\partial Z'}{\partial X} - i \frac{\partial Z''}{\partial X} \right) \quad (53)$$

is maximal. For example, see Figure 13.

3. Instrumentation

3.1. Introduction

The obviously singular relation between a sinusoidal perturbation applied to an object and its first-order response can be measured in several ways, which are more or less different in principle. The response having two characteristics, one may choose either amplitude and phase angle, or in-phase and quadrature component as the output data. As opposed to other relaxation methods, a galvanostatic approach (a.c. current control) is equivalent to a potentiostatic approach (a.c. voltage control), the difference being only of a

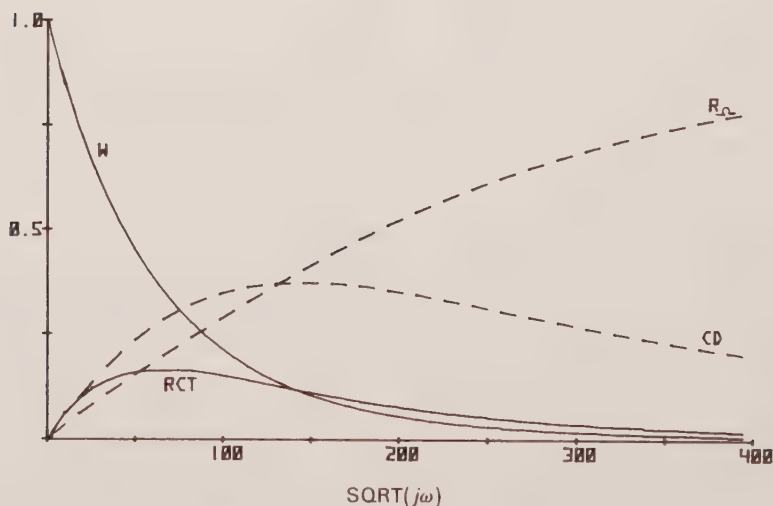


Figure 13. Relative information to be obtained from measured impedances. $R_{\Omega} = 1 \Omega \text{ cm}^2$, $C_d = 20 \mu\text{F cm}^{-2}$, $R_{ct} = 1 \Omega \text{ cm}^2$, $\sigma = 200 \Omega \text{ cm}^2 \text{ s}^{-1/2}$.

technical nature. It may be noted that the concept "potentiostatic" is somewhat misleading, because it is usually not feasible really to control the interfacial potential, but only the potential difference between the working electrode and a suitable reference electrode.

This section will not yield complete descriptions of instrumental details, nor a complete survey of all apparatus which have been constructed in the past. Instead, we will attempt to outline general features, based on the (possible) demands of the experimentalist on one side and on the potentialities and limitations of the methods on the other side.

For detailed earlier reviews interested readers are referred to references (37), (38), and (7).

3.2. Theoretical Constraints

The precision of the data analysis discussed at the end of section 2 depends on the following aspects.

(i) *Amplitude accuracy.* To minimize the error in the impedance or admittance one can either fix the input amplitude and measure the output accurately, or measure both accurately and divide. Calibration is simply done by replacing the object by a standard precision resistor.

(ii) *Phase accuracy.* A possible error in the measured phase angle is more critical. For small deviations, $\Delta\phi$, $\Delta Z'$, $\Delta Z''$, from the correct values one has, cf. Eqs. (4), (5), in first approximation:

$$\frac{\Delta Z'}{Z'} = \frac{1}{Z'} \frac{dZ'}{d\phi} \Delta\phi = -\frac{Z''}{Z'} \Delta\phi = -\tan \phi \times \Delta\phi \quad (54)$$

$$\frac{\Delta Z''}{Z''} = \frac{1}{Z''} \frac{dZ''}{d\phi} \Delta\phi = \frac{Z'}{Z''} \Delta\phi = \cot \phi \times \Delta\phi \quad (55)$$

For the Randles circuit ϕ decreases from a value between $\pi/2$ and $\pi/4$ to zero when the frequency increases to infinity. This means that the error in Z' decreases and the error in Z'' increases with frequency. Therefore the magnitude of ϕ in the extreme parts of the frequency range imposes the acceptable phase error. To give an idea, when $\cot \phi = 10$, an error of 0.003 rad (0.2°) causes an error of 3% in Z'' .

When a device essentially measures directly the components, similar arguments as above hold, since then the phase accuracy is connected to the correlation between input and reference signal.

(iii) *Accuracy of the d.c. variable.* Strictly, either d.c. current or d.c. potential may be used as the d.c. coordinate, since of course the two are interdependent. However, from the experimental point of view, accurate measurement of the faradaic d.c. current is often affected by residual currents due to impurities and (sometimes) double layer charging. Therefore it is common use to measure impedances or a.c. currents as a function of the d.c.

potential, which is referred to a (measured or calculated) reference potential, e.g., the standard or the reversible half-wave potential [cf. Eqs. (43) to (46)].

Mostly the demand for a well-defined imposed potential is encountered by the application of solid-state potentiostats. A precision of 1 mV is usually sufficient, as can be derived from the potential dependence of Z_F .

(iv) *Dynamic range and bandwidth.* One important item not discussed thus far is the order of magnitude of the perturbing signal. When the perturbation is single-harmonic, $A_m \sin \omega t$, the higher order terms in the Taylor expansion of the response [eqs. (7), (9)] contain essentially the corresponding powers of $\sin \omega t$, $\cos \omega t$, or their products. In view of the trigonometric relations

$$\sin \omega t \cos \omega t = (1/2) \sin 2\omega t \quad (56a)$$

$$\sin^2 \omega t = 1 - \cos^2 \omega t = (1/2)(1 - \cos 2\omega t) \quad (56b)$$

$$\sin^3 \omega t = (3/4) \sin \omega t - (1/4) \sin 3\omega t \quad (56c)$$

$$\cos^3 \omega t = (3/4) \cos \omega t + (1/4) \cos 3\omega t, \text{ etc.} \quad (56d)$$

it can be seen that the third-order response contributes to the signal measured at the fundamental frequency. The same holds for higher odd orders.

Therefore, identification of an output with the first-order response requires two conditions:

- (a) The measuring device should select the fundamental frequency with sufficient rejection of the harmonics
- (b) The input amplitude should be so small that the third and higher odd order contributions to the fundamental frequency output are negligible.

The limit beyond which the second condition is obeyed is different for different circumstances, e.g., choice of d.c. potential, reversibility (see Figure 14). Generally, the experiment is considered to be "safe," when the amplitude of the a.c. potential does not exceed $5/n$ mV.⁽³⁹⁾

It seems seldomly recognized that this rule concerns the potential difference *across the interface*, i.e., the voltage across the cell minus the voltage across the ohmic resistance. In Figure 15, it is shown how far the total cell voltage may exceed the above-mentioned limit, especially at high frequencies.

It should also be noted that experiments at large amplitudes are not at all useless, but only theoretically more difficult to handle. When the theory is restricted to cases with negligible charge transfer control, it is possible to derive a rather elegant expression which closely approximates the exact faradaic fundamental harmonic current raised by an a.c. potential $E_{a.c.} = (RT/nF)\Psi \cos \omega t$.⁽⁴⁰⁾ It appears to consist of an "alternative" formulation of

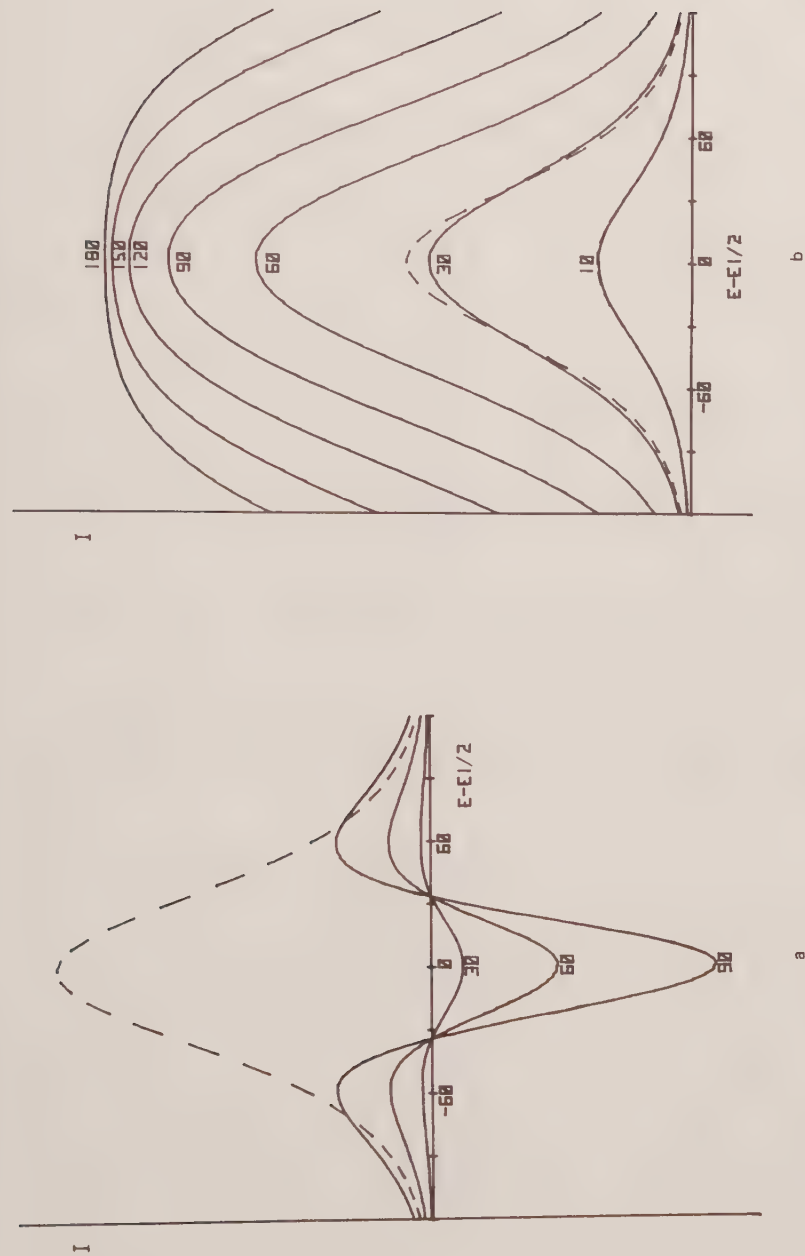


Figure 14. (a) Relative contributions of first-order (dashed curve) and third-order (solid curves) responses to the fundamental harmonic current as a function of d.c. potential. Reversible electrode reaction. Arbitrary scale units. (b) Total fundamental harmonic current amplitude for large voltage amplitudes; cf. Eq. (57), dashed curve; cf. Eq. (44), solid curves; solid curves indicate a.c. voltage amplitudes in mV.

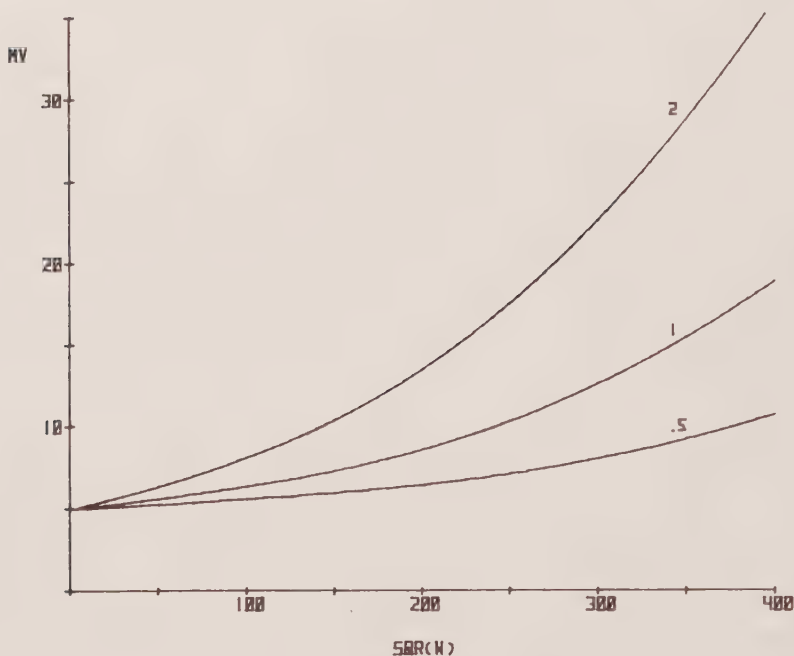


Figure 15. Total a.c. voltage required to produce a 5-mV interfacial voltage, as a function of frequency. Components of the Randles circuit: $C_d = 20 \mu\text{F cm}^{-2}$, $R_{ct} = 1 \Omega \text{ cm}^2$, $\sigma = 200 \Omega \text{ cm}^2 \text{ s}^{-1/2}$, and $R_\Omega = 0.5, 1, 2 \Omega \text{ cm}^2$ (indicated).

the Warburg coefficient:

$$\frac{1}{\sigma} = \frac{nF}{4} (c_O^* D_O^{1/2} + c_R^* D_R^{1/2}) (2\omega)^{1/2} \times \left\{ \frac{\exp(2\Psi) - 1}{1 + [\exp \zeta + \exp(-\zeta)][\exp(\Psi) + \exp(2\Psi)]} + \frac{[\exp(\Psi 2^{1/2}) - 1] 2^{1/2}}{1 + [\exp \zeta + \exp(-\zeta)] \exp(\Psi/2^{1/2}) + \exp(\Psi 2^{1/2})} \right\} \quad (57)$$

Properties of this “ σ ” are shown in Figure 14.

(v) *Tuning*. Small-amplitude experiments naturally suffer more from spurious noise signals. Even more than condition (a) this necessitates tuning of the detector to the selected frequency with a narrow band-width.

However, in tuning devices (with filters), constraining the bandwidth involves the disadvantage of extending the time constant of the instruments. In other words, the narrower the bandwidth, the more time is needed to indicate the proper response value after perturbation. Of course this is a serious limitation when either the perturbation signal or the response signal changes at a high rate.

3.3. The Object

The evolution of electronics during the last two decades is of great importance for the facility in experimentation with special objects. The following remarks can be made.

3.3.1. Stationary and Nonstationary Objects

In the context of this chapter, an object may be defined as stationary when its impedance is independent of time. Potential examples: rotating disk electrodes, (thin-layer) twin electrode cells, and planar electrodes with constant area, the latter only in the d.c. reversible case. Examples of the opposite: the dropping mercury electrode (DME), spherical or cylindrical electrodes, and planar electrodes in the d.c. irreversible case.

Of course the DME is a special object, its time dependence being very pronounced, so that either recording of the entire response during drop-life or sampling at a particular time is badly needed. Yet the use of a DME is highly recommended both in analytical a.c. polarography and in fundamental investigations. The reasons: the splendid reproducibility of the surface, the wide range of applicability, but especially the opportunity for d.c. polarization, the importance of which has been shown in Section 2. In fact comparable profits are only present at a constant area electrode which is d.c. polarized by a fast potential sweep, although theoretical complications demand more calculational effort.⁽⁴¹⁾

Perhaps a more trivial class of nonstationary objects are those at which the conditions at the surface change in time due to some spurious or non-spurious effects, e.g., progressive poisoning, disintegration, or adhesion of reaction products. Also, in these cases, recording or sampling is necessary.

3.3.2. Spurious Frequency Dispersion

The theory requires that, in the absence of a faradaic process, $Z' (= R_\Omega)$ and $\omega/Z'' (= C_d)$ are frequency independent. In practice, however, often a (slight) frequency dependency is observed. This is ascribed to different causes: for mercury electrodes, shielding by the glass edge of the support (e.g., the capillary of the DME);⁽⁴²⁾ for solid electrodes roughness of the surface.^(43,44)

The effects are revealed as an increase of the apparent R_Ω and C_d on going to lower frequencies, but it can also be seen as an additional interfacial admittance.⁴⁵ Neglect of these effects will obviously introduce errors in data analysis, despite that sometimes a correction procedure seems possible.

Another source of unwanted frequency dispersion is in principle the geometric capacity of the two electrodes and the electrolyte as a dielectric in between. Almost always this is forgotten but it is questionable whether this is reasonable for low conductances and high frequencies. In this case the effect is an apparent increase of C_d at increasing frequency (Figure 16).

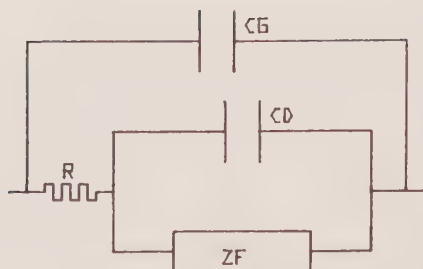


Figure 16. Equivalent circuit including geometric capacity C_G . Other symbols the same as in Figure 2.

3.3.3. The Purpose

Apart from the restrictions, the choice of input variables is ruled by what is aimed at. As in Section 1 we distinguish roughly the following fields:

- (a) Characterization of electrochemical systems in terms of models: frequency range as wide as possible, amplitude restricted to first-order response. Even the above-mentioned "geometrical" effects may be the centre of interest instead of being spurious, e.g., in the case of porous electrodes.⁽⁴⁴⁾
- (b) Quantitative compound analysis: conditions standardized, i.e., one or more particular frequencies, at which sensitivity is maximal and where preferably reversible behavior exists; amplitude not necessarily limited, unless with a view to resolution.
- (c) Investigation of a particular process, e.g., charge transfer: frequency range providing the maximal information, amplitude restricted, and moreover, utmost elimination of spurious effects.

Generally, in these cases the optimal frequencies fall in the audio-range (say 30–30,000 Hz), where relatively low demands are made upon modern electronic design. Outside this range more care should be taken, especially at the extremely low frequencies sometimes applied (down to 0.001 Hz). Note that the time of measurement is at least $2\pi/\omega$, but usually longer because of transient behavior. Moreover, tuning at low frequencies requires filtering with long time constants, which may especially interfere with the correct treatment of nonstationary systems.

3.3.4. Separation of Faradaic and Nonfaradaic Contributions

The procedure in Section 2.6 to subtract R_n from the total impedance and C_d from the electrode admittance may be called a mathematical or "digital" procedure. Another procedure, to be called "analog," is possible in the following way:

Two cells are constructed in exactly the same way, one containing the solution of interest, the other the same solution without the electroactive

component(s). Both cells are supplied with the same a.c. and d.c. voltage by means of a potentiostat equipped with a positive feedback path, which subtracts the ohmic drop electronically. The resulting currents (corresponding to the *electrode* admittance) are electronically subtracted from each other to yield the pure faradaic current.⁽⁴⁶⁾

This method is mainly useful for analytical purposes, because of the automatic character. For more fundamental studies, its use should be discouraged because the profits are less than the risks of miscompensation. The awareness of this will become apparent from the brief survey of the most important techniques in the following.

3.4. Steady State Measurements

3.4.1. A.C. Bridges

The principle is classical:⁽⁴⁷⁾ the unknown impedance is matched by a known one, constructed of a variable resistance and a variable capacitance of precision quality, in a circuit shown in Figure 17, following the rules given in the legend. The matching network may be either a series connection (R_s, C_s) or a parallel connection (R_p, C_p). The latter has advantages for highly capacitive systems, because then in the (R_s, C_s) configuration a high C_s setting would be required, beyond what is available in commercial capacitance boxes.

The bridge of Figure 17 is most commonly used, both for double layer and kinetic studies. For high precision or extreme frequencies, other configurations have been developed, cf. Figures 18 and 19. For principles see also reference 38. The method is essentially neither galvanostatic nor potentiostatic, i.e., the a.c. input need not be stabilized. However, especially for kinetic studies, a stabilized d.c. input is very important. This is hardly to be realized

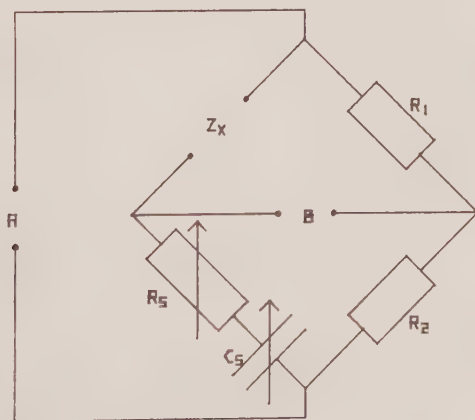


Figure 17. Wien bridge (schematic) for audio-frequency measurements. R_1, R_2 , ratio arm resistors; R_s, C_s , matching impedance (see also text). Terminals: A, a.c. input; B, output to detector and d.c. input in series.^{(18),(33)} Balance equation: $Z_x/Z_s = R_1/R_2$.

in the classical configuration, because connecting the d.c. input terminals in Figure 17 to a modern potentiostat leads to grounding problems and oscillation.

A better solution is to make the potentiostat itself the main part of the bridge⁽⁵⁰⁾ (see Figure 20). Variations to this principle are also possible. With bridges of this type, one can obtain high d.c. potential stability, but also high amplitude and phase accuracy in a wide frequency range.

Automatically balancing bridges, like the Wayne and Kerr, operate on only a very limited number of frequencies and are too slow to follow the variation of the impedance of the DME accurately.

3.4.2. Direct Measurements

Two disadvantages of bridge performance, viz. manual operation and relatively poor noise rejection, are (partly) avoided in direct measurements: the object is perturbed by a stabilized input (potentiostatic or galvanostatic) and the response is read on a phase-sensitive detector (lock-in amplifier).

The better noise rejection is inherent to the principle of the lock-in amplifier,⁽⁷⁾ which is as follows: the perturbing signal $A = A_m \sin \omega t$, is used as a reference voltage which is multiplied by the response signal, $B = B_m \sin(\omega t + \phi)$. The d.c. component of this product is displayed. Following Eqs. (56a) and (56b), this results in the indication of the in-phase component of B . For the quadrature component the reference signal is first shifted over 90° . Ideally this procedure, called correlation, discriminates all other signals supplied to the amplifier. However, this gain is obtained at the expense of a worse precision, inherent to analog scale readings, relative to a compensation method. Moreover, the required phase accuracy (Section 3.2) puts high demands on the electronics of the device.

3.4.3. A.C. Polarographs

When dealing with nonstationary objects, graphical or digital recording versus time is necessary. When the a.c. current response of Figure 21b is recorded versus d.c. potential, one obtains a modern phase-selective a.c.

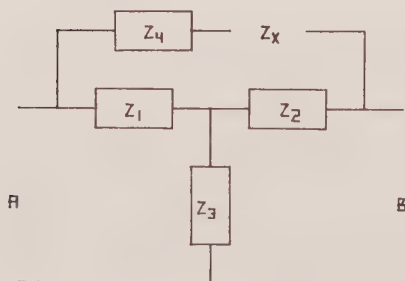


Figure 18. T-bridge (schematic) for high frequency measurements.⁽⁴⁸⁾ Z_1 , Z_2 , Z_3 , Z_4 : impedances containing resistors, capacitors, and self-inductances. Terminals: A, a.c. + d.c. input; B, output to detector. Balance equation: $(Z_4 + Z_x) + Z_1 + Z_2 + Z_1 Z_2 / Z_3 = 0$. Measurements are performed comparatively, replacing Z_x by a known impedance (RC = series connection).

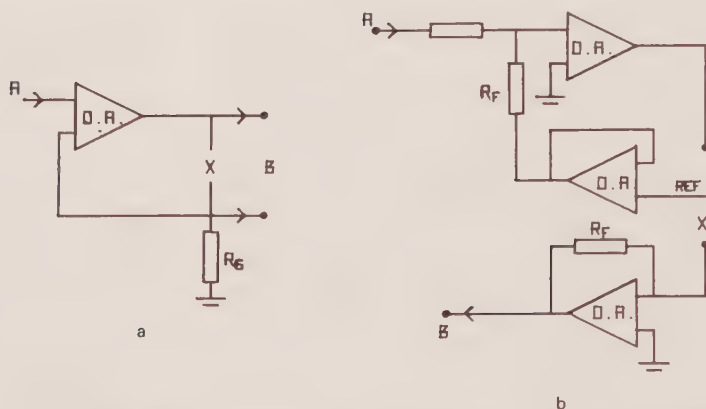


Figure 21. (a) Galvanostatic arrangement, (b) potentiostatic arrangement. O.A., operational amplifiers; R_G , current limiting resistor ($R_G \gg Z_x$), R_F , feedback resistors. Terminals: A, d.c. + a.c. input; B, d.c. + a.c. output to phase-sensitive measuring device.

3.4.4. Computerization

The availability of relatively low-cost, highly sophisticated minicomputers justify a consideration of what their profits may be in the performance of a.c. experiments:

- (a) Programming. Especially with nonstationary objects it is necessary either to repeat a whole series of measurements at different potentials and frequencies several times (long-range time dependence) or to sample the output at a well-defined moment (DME).
- (b) Data acquisition. The abundance of resulting data should be averaged and stored in an accessible way, e.g., on punchcards, or paper or magnetic tape.
- (c) Fitting analysis. Numerous calculations are necessary to obtain final results, and to estimate their reliability and precision.

As an example, in Figure 22 a block diagram is given of a modular Network Analyzer System, composed of commercially available parts and especially dedicated to measurements at a DME.⁽⁵³⁾ The actions, automatically performable, are:

- (1) Dictating a.c. input; a.c. source: frequency 0–13 MHz, resolution 1 to 1000 Hz, and amplitude –70 to +26 Dbm, resolution 0.1 Dbm.
- (2) Dictating d.c. input: –10 to +10 V, resolution 1 mV.
- (3) Alternative switching to cell or dummy cell, with appropriate connection or disconnection of inputs, to allow zero drift correction.
- (4) Receiving a trigger signal from the drop fall detector via a time delay.

The very essential corrections for system errors [mentioned under (7)] include all analog errors (both amplitude and phase errors) in the potentiostat and the network analyzer, the correction data being stored in the calculator memory.

3.5. Transient Measurements; The Fast Fourier Transform

3.5.1. Laplace and Fourier Transforms

Generally the operation called Laplace transformation can be considered as the conversion of a function $F(t)$, existing in the "time domain" to a function $f(s)$, existing in the "frequency domain", where the parameter s , indicated as "frequency", may be real, imaginary, or complex.

The relative simplicity of current-potential relations in the frequency domain, as compared with the corresponding relations in the time domain, has led to the introduction of Laplace Plane Analysis of results of transient relaxation techniques (i.e., perturbation by current step, current impulse, or potential step, etc.).^(54,55,56) This method, long known in operations research, network analysis, and control theory, is based on the definition of the operational impedance or transfer function.

$$Z(s) = \frac{\bar{V}(s)}{\bar{I}(s)} = \frac{\mathcal{L}V(t)}{\mathcal{L}I(t)} \quad (58)$$

Briefly, the possible versions are:

- a1. The response, obtained as a set of data points is transformed numerically, whereas the perturbation is considered as a known (controlled) function $P(t)$ which can be transformed analytically⁽⁵⁵⁾
- a2. Both response and perturbation are considered as measured quantities (as a function of time) and are transformed numerically⁽⁵⁶⁾
- a3. The perturbation is considered as a known function $P(t)$ and the response data are fitted to an empirical function $R(t)$, whereafter both are transformed analytically⁽⁵⁸⁾
- b1. The Laplace parameter is taken real, s
- b2. The Laplace parameter is taken complex, $s + j\omega$
- b3. The Laplace parameter is taken imaginary, $j\omega$

For a detailed discussion see Reference 57.

The alternative b3 is essentially the one-sided Fourier transform, e.g., of a function $s(t)$:

$$S(f) = \int_0^{\infty} s(t) \exp(-i2\pi ft) dt \quad (59)$$

Performance of this integral for both $s(t) = V(t)$ and $s(t) = I(t)$ allows the complex impedance to be obtained from an experiment with an arbitrarily chosen input function. Strictly, when applied to a1 or a2, the data sets should be extrapolated to $t = \infty$, because otherwise the integral is undefined. In case a3, this problem is avoided by dividing the analytical transforms following Eq. (58). It can be argued,⁽⁵⁷⁾ however, that $s(t = \infty)$ will have a steady state value, the transform of which can be added to the numerical transform.

3.5.2. The Discrete Fourier Transform (DFT)

Instead of an algorithm for continuous numerical integration of Eq. (59) (almost a contradiction), the integral may be replaced by a summation:

$$S(f_m) = \sum_{n=0}^{N-1} s(t_n) \exp(-i2\pi f_m t_n) \times (t_{n+1} - t_n) \quad (60)$$

or

$$S(m\Delta f) = \Delta t \sum_{n=0}^{N-1} s(n\Delta t) \exp(-i2\pi m\Delta f n\Delta t) \quad (m \leq N/2) \quad (61)$$

which means that N data samples in the time domain spaced by an interval Δt are transformed to yield $N/2$ data points in the frequency domain. This operation is called the Discrete Fourier Transform. It has obtained considerable importance because it is most suitable for efficient computer calculations via algorithms known as the Fast Fourier Transform (FFT);⁽⁵⁹⁾ for further readings, see, e.g., reference (60). Application in electrochemistry was introduced by Creason, Hayes, and Smith⁽⁶¹⁾ in the form of a home-built on-line computerized system. Commercial Fourier-analyzers are also available.

3.5.3. Potentialities

The performance of Eq. (61) involves the time domain parameters Δt , N , and $T = N\Delta t$, and the frequency domain parameters Δf , $N/2$, and $F_{\max} = (N/2)\Delta f$, where T is the duration of the signal and $F_{\max}$ the maximum frequency to be resolved. These parameters are related by Shannon's sampling theorem which says that it requires *slightly more* than two samples per period to uniquely define a sinusoid. The relations are then

$$(N/2)\Delta f = F_{\max} = 1/2\Delta t \quad (62)$$

$$\Delta f = 1/N\Delta t = 1/T \quad (63)$$

The application of FFT provides different possibilities to obtain high-precision information on a system's properties. Briefly summarized for a

perturbation $x(t)$ and a response $y(t)$:

- (a) DFT of $X(t) \rightarrow X(f)$; DFT of $y(t) \rightarrow Y(f)$; $Y(f)/X(f) = Z(f)$
- (b) Auto-correlation: $G_{xx} = X(f) \cdot X^*(f)$; $G_{yy} = Y(f) \cdot Y^*(f)$;
 $G_{yy}(f)/G_{xx}(f) = Z(f)^2$
- (c) Cross-correlation: $G_{yx} = Y(f) \cdot X^*(f)$; $G_{yx}(f)/G_{xx}(f) = Z(f)$ (N.B. X^* , Y^* = complex conjugate of X , Y , respectively.) Operation c (cross power spectrum) allows noise rejection by ensemble averaging.
- (d) Coherence function: $G_{yx}^2/(G_{xx} \cdot G_{yy})$, which should be unity if noise is absent, and thus provides a check of proper noise rejection.
- (e) Digital filtering, i.e., multiplying a function $S(f)$ by the transfer function $H(f)$ of a hypothetical filter: $S'(f) = S(f) \cdot H(f)$.

3.5.4. Limitations

Due to the discontinuous character of DFT, errors may slip into the result, which require special precaution:

(a) Leakage (window error): Sampling N data points of a function $s(t)$ in a period T can be seen as looking at the function through a "time window". When $s(t)$ contains a sinusoidal component of frequency f_0 , there are two situations possible: either the periodic component has an integral number of periods in the window ($T = n/f_0$) or it has not. In the latter case the singular component in the time domain will show up as a number of components in the frequency domain, thus giving a false impression of $s(t)$. This error may be suppressed, though with loss of resolution, by using a more sophisticated DFT procedure, which essentially modifies the shape of the time window (Hanning window).

(b) Aliasing: When $s(t)$ contains a periodic component with frequency exceeding $F_{\max}$, e.g. $F_{\max} + F$, this component is sampled at a too low rate. The result is an apparent component in the frequency domain at $F_{\max} - F$. Therefore one should either adjust the sampling rate to the highest frequencies present, or cut frequencies above $F_{\max}$ by means of an *analog* filter.

As will be obvious, application of FFT in electrochemistry requires only a source of excitation, a device which samples both excitation and response and stores the data in a memory (transient recorder), and an interfacing of this device with a computer. The attractive feature is that it is possible to obtain the impedance spectrum (obeying relatively simple algebra) in one measurement of, e.g., the response to a step perturbation. However, it is not generally recognized that in this way one withdraws one advantage of analog measurements, viz. the rejection of higher harmonics generated by the non-linear cell. When this is to be avoided, e.g., in precision measurements, a so-called "pseudo-random waveform" may be applied, which is a composition of a limited number of sinusoidal components with frequencies $f, 3f, 5f \dots$ (odd harmonic series) and with randomized phases.⁽⁶²⁾

4. Second-order Techniques

4.1. Introduction

One may wonder to what extent it is worthwhile to dedicate a special section to the so-called second-order a.c. techniques apart from the much more widely applied first-order periodic techniques and transient relaxation techniques. The present state of affairs may be characterized as follows:

- *Applications in the fundamental field* have almost been restricted to the determination of the charge transfer parameters (rate constant, transfer coefficient) with the aid of the faradaic rectification method. Most of the literature can be traced to Doss and Agarwal (the inventors), Delahay, Barker, and Sluyters [for references, see reference (63)]. Very often the results are discrepant from results obtained by other methods.
- *Applications in analytical chemistry* are not numerous, but nevertheless many variants of second-order principles such as second-harmonic polarography, modulation, demodulation, and intermodulation polarography, have been elaborated, at least instrumentally.^(23,64,65,66,67,68) Due to recent progress in electronics and digital manipulation, a tendency of renewed interest in finding other variants is perceptible.
- *The theory* underlying all this may be called chaotic in the sense that derivations of characteristic current-voltage relations are always devoted to the variant of interest, sometimes restricted to the faradaic process, sometimes also including double layer charging. Only Rangarajan^(69,83) has presented a "unified" theory, written as a very general and fundamental formalism, but not very accessible for the inexperienced reader.
- *The direct determination* of a second-order effect is only possible via perturbation with a *periodic* signal, which itself can be more or less complex. Depending on this complexity, a larger or smaller number of criteria can be selected that are representative for the second-order contributions to the response. This puts more or less high demands on instrumentation and, due to the dominating role of the first-order response, these demands will usually be higher than for the first-order methods.

The outlines above justify the conclusion that a general and uniform treatment of the second-order phenomena might be useful, in the first place to examine the non-linear nature of the electrochemical cell and the information therein enclosed, and in the second place to envisage the applicability in practice (the advantages and disadvantages) with respect to the linear methods.

To this end we will consider both charge transfer aspects (Section 4.2) and mass transfer aspects in a general way, the latter distinguished for a.c. potential control (Section 4.3) as well as a.c. current control (Section 4.4).

4.2. First- and Second-order System Parameters Considered from a Thermodynamic Point of View

First we will consider the subject in a very formal way, following the elegant treatment of Reinmuth.⁽²⁶⁾ The essential feature is that instead of assuming an explicit current-potential-concentration relationship, e.g., the absolute rate equation, a quite formal expansion in terms of partial derivatives is performed. Although this may lead to more complex system descriptions than actually were needed, it establishes exactly what kind of information may be expected from first- and second-order experiments.

4.2.1. Expansion of the Faradaic Current

Suppose the electrochemical system, containing a single electro-active couple, is initially at equilibrium, so that Nernst's law holds: $c_O^*/c_R^* = \exp \varphi_i$ with $\varphi_i = nF/RT(E_i - E^\circ)$. When this system is perturbed, a faradaic current will flow with a current density j_F , which is a function of $c_O = c_O^* + \Delta c_O$, $c_R = c_R^* + \Delta c_R$, and $\varphi = \varphi_i + \varepsilon$ [$\varepsilon = (nF/RT)\Delta E$]. Expansion of j_F in a Taylor series around the equilibrium situation $j_F(c_O^*, c_R^*, \varphi_i) = 0$, describes j_F as

$$j_F = \sum_{k=1}^{\infty} (1/k!)[\Delta c_O(\partial/\partial c_O) + \Delta c_R(\partial/\partial c_R) + \varepsilon(\partial/\partial \varphi)]^k j_F \quad (64)$$

where $(\partial/\partial x)^k$ denotes the *partial* k^{th} derivative with respect to x , at $E = E_i$.

Now it is imaginable that a set of separate perturbations Δc_O , Δc_R , and ε is applied such that the result is a *new equilibrium* situation, i.e., $j_F = 0$. According to Nernst's law these perturbations must be related by

$$\begin{aligned} \left(1 + \frac{\Delta c_O}{c_O^*}\right) &= \left(1 + \frac{\Delta c_R}{c_R^*}\right) \exp \varepsilon \\ &= \left(1 + \frac{\Delta c_R}{c_R^*}\right) \left(1 + \sum_{m=1}^{\infty} \frac{\varepsilon^m}{m!}\right) \quad \text{for } j_F = 0 \end{aligned} \quad (65)$$

Equation (64) being completely general, the special case represented by Eq. (65) imposes special relationships between the partial derivatives in Eq. (64). Keeping the expansions limited to first order we obtain after introduction of Eq. (65) into Eq. (64), with $j_F = 0$:

$$0 = [c_O^*(\partial j_F/\partial c_O) + (\partial j_F/\partial \varphi)]\varepsilon + [(c_O^*/c_R^*)(\partial j_F/\partial c_O) + (\partial j_F/\partial c_R)]\Delta c_R \quad (66)$$

Since this must be valid for any mutually independent values of ε and Δc_R , it follows that the coefficients of ε and Δc_R must be zero. So

$$c_O^*(\partial j_F/\partial c_O) = -c_R^*(\partial j_F/\partial c_R) = -\partial j_F/\partial \varphi \quad (67)$$

Consequently the first-order approximation of Eq. (64) becomes

$$j_F(1) = (\partial j_F/\partial \varphi)[\varepsilon + (\Delta c_R/c_R^*) - (\Delta c_O/c_O^*)] \quad (68)$$

In this way an equation quite identical to Eq. (28) has been derived *without* specification of a rate equation for charge transfer.⁽⁷⁰⁾ Evidently, the equation has one "operational" charge transfer parameter, $\partial j_F / \partial \varphi$, which is equivalent to the "exchange current density" I_0 in the absolute rate theory. However, in the context of the present considerations, $\partial j_F / \partial \varphi$ is open for any interpretation in terms of a model, to be verified by determining its dependence on initial circumstances (potential, concentration, etc.).

Proceeding in a similar way for the second-order approximations of both Eqs. (64) and (65), three relations are obtained between the six second partial derivatives, composing the *total* second-order approximation as

$$j_F(2) = j_F(1) + \widetilde{FF} \cdot \varepsilon^2/2 + \widetilde{OF} \cdot \varepsilon \Delta c_O + \widetilde{RF} \cdot \varepsilon \Delta c_R \\ + \widetilde{OO} \cdot \Delta c_O^2/2 + \widetilde{RR} \cdot \Delta c_R^2/2 + \widetilde{OR} \cdot \Delta c_O \Delta c_R \quad (69)$$

The meaning of $\widetilde{FF}$, $\widetilde{OF}$, etc., and the above-mentioned relations are given in Table 5. Evidently the relations involve the first-order parameter, which suggests the introduction of the "abbreviations" in the third column, which are chosen such that their meaning corresponds to the absolute rate theory when the latter is applicable.⁽²⁶⁾

It may be noted that $\widetilde{OO}$, $\widetilde{RR}$ and $\widetilde{OR}$ will have finite values only when the act of charge transfer does not obey first-order kinetics with respect to the concentrations of *Ox* and *Red* (outside the double layer). In this respect ν_O and ν_R in Table 5 may be considered as "stoichiometric numbers".

4.2.2. Expansion of the Interfacial Potential

Equation (69) is in a form suitable for application to the theories of techniques in which the potential is controlled and the current observed. In the converse situation, it is more obvious to have an expansion of φ in terms of j_F , c_O , and c_R :

$$\varepsilon = \sum_{k=1}^{\infty} (1/k!) [j_F(\partial/\partial j_F) + \Delta c_O(\partial/\partial c_O) + \Delta c_R(\partial/\partial c_R)]^k \varphi \text{ at } E = E_i \quad (70)$$

This can be combined with the alternative expansion of the Nernst equation [cf Eq. (65)]:

$$\varepsilon = \ln(1 + \Delta c_O/c_O^*) - \ln(1 + \Delta c_R/c_R^*) \\ = - \sum_{m=1}^{\infty} (1/m)(-\Delta c_O/c_O^*)^m + \sum_{m=1}^{\infty} (1/m)(-\Delta c_R/c_R^*)^m \quad (71)$$

Similar manipulations as above lead to the formal relationships collected in Table 5, where in addition the mathematical connections with the current derivatives are given. The whole treatment leads to the *complete* second-order

Table 5
Second-order Operational Parameters Following Reinmuth's Treatment

A.C. potential control ^a			A.C. current control ^b				
Partial derivative	Shorthand notation	Meaning in ART ^c	Relationship	Partial derivative	Shorthand notation	Meaning in ART	Relationship
$\delta^2 j / \delta \phi^2$	$\overline{FF}$	$I_0(1 - 2\alpha)$		$\delta^2 \phi / \delta j^2$	$\frac{\overline{FF}}{I_0^3}$	$\frac{2\alpha - 1}{I_0^2}$	$= - \frac{\partial^2 j / \partial \phi^2}{\partial j / \partial \phi}$
$\delta^2 j / \delta c_O^2$	$\overline{OO}$	$\frac{I_0(1 - \nu_O)}{(c_O^*)^2}$		$\delta^2 \phi / \delta c_O^2$			$= - \frac{1}{(c_O^*)^2}$
$\delta^2 j / \delta c_R^2$	$\overline{RR}$	$\frac{I_0(\nu_R - 1)}{(c_R^*)^2}$		$\delta^2 \phi / \delta c_R^2$			$= \frac{1}{(c_R^*)^2}$
$\delta^2 j / \delta c_O \delta c_R$	$\overline{OR}$	$\frac{I_0(\nu_R - \nu_O)}{2c_O^* c_R^*}$	$\overline{OR} = - \frac{\overline{OO}(c_O^*)^2 + \overline{RR}(c_R^*)^2}{2c_O^* c_R^*}$	$\delta^2 \phi / \delta c_O \delta c_R$			$= 0$
$\delta^2 j / \delta c_O \delta \phi$	$\overline{OF}$	$\frac{I_0(2\alpha - 1 + \nu_O)}{2c_O^*}$	$\overline{OF} = \frac{I_0 - \overline{OO}(c_O^*)^2 - \overline{FF}}{2c_O^*}$	$\delta^2 \phi / \delta c_O \delta j$	$\frac{\overline{OF}}{I_0^2}$	$\frac{1 - 2\alpha - \nu_O}{2I_0 c_O^*}$	$= - \frac{\partial^2 j / \partial c_O \partial \phi}{(\partial j / \partial \phi)^2}$
$\delta^2 j / \delta c_R \delta \phi$	$\overline{RF}$	$\frac{I_0(1 - 2\alpha + \nu_R)}{2c_R^*}$	$\overline{RF} = \frac{I_0 + \overline{RR}(c_R^*)^2 + \overline{FF}}{2c_R^*}$	$\delta^2 \phi / \delta c_R \delta j$	$\frac{\overline{RF}}{I_0^2}$	$\frac{2\alpha - 1 - \nu_R}{2I_0 c_R^*}$	$= - \frac{\partial^2 j / \partial c_R \partial \phi}{(\partial j / \partial \phi)^2}$

^a cf. Eq. (69). ^b cf. Eq. 72. ^c $I_0 = (RT/nF)/R_{ex}$ = "Exchange current density", α = "transfer coefficient", ν_O , ν_R = "stoichiometric numbers".

approximation of φ in the form:

$$\begin{aligned} \varepsilon(2) = & j_F/I_0 + \Delta c_O/c_O^* - \Delta c_R/c_R^* - \frac{1}{2}(\Delta c_O/c_O^*)^2 + \frac{1}{2}(\Delta c_R/c_R^*)^2 \\ & + \frac{1}{2}(\widetilde{FF}/I_0^2)j_F^2 - (\widetilde{OF}/I_0^2)j_F\Delta c_O \\ & - (\widetilde{RF}/I_0^2)j_F\Delta c_R \end{aligned} \quad (72)$$

4.3. A.C. Potential Control

The foregoing section, being general with respect to the model, is restricted to *initial equilibrium conditions*. Our purpose here is to obtain the second-order current response to a given (periodic) potential perturbation superimposed on an arbitrary d.c. potential, i.e., under *nonequilibrium conditions*. As we did for the impedance (Section 2) we will adopt the absolute rate equation [Eq. (27)] for illustration, but make the derivations as general as possible, so that replacement by another model is easy. In a way, our reasonings are explicit elaborations of the formal treatments of Rangarajan,⁽⁶⁹⁾ although sacrificing part of the elegant generalism of this theory.

4.3.1. Expansion

Performing the Taylor expansion as in Section 4.2, but now around the situation at the d.c. mean potential, one obtains in "short-hand notation":

$$\begin{aligned} j_F - j_{F,d.c.} = \Delta j_F = & \tilde{F} \cdot \varepsilon + \tilde{O} \cdot \Delta c_O + \tilde{R} \cdot \Delta c_R \\ & + \widetilde{FF} \cdot \varepsilon^2/2 + [\widetilde{OF} \cdot \Delta c_O + \widetilde{RF} \cdot \Delta c_R] \varepsilon \\ & + \widetilde{OO} \cdot \Delta c_O^2/2 + \widetilde{RR} \cdot \Delta c_R^2/2 + \widetilde{OR} \cdot \Delta c_O \Delta c_R \end{aligned} \quad (73)$$

The meaning of the partial derivatives in the absolute rate theory is given in Table 6. Note that $-\alpha = d \ln k_f / d\varphi$ and $-\alpha' = d^2 \ln k_f / d\varphi^2$ are *operational* parameters.

Now, when ε is a dictated function, the problem is to eliminate the unknown Δc 's. Anticipating that the current will be composed of additive contributions of different order:

$$\Delta j_F = \Delta j_{F,1} + \Delta j_{F,2} + \cdots + \Delta j_{F,N} \quad (74)$$

it can also be anticipated that the surface concentrations are related to the current by operators⁽⁶⁹⁾ expandable in an N^{th} order series:

$$\Delta c_O = \frac{1}{nFD_O^{1/2}} \tilde{\gamma}_O(\Delta j_F) = \frac{1}{nFD_O^{1/2}} [\tilde{\gamma}_{O,1} + \tilde{\gamma}_{O,2} + \cdots + \tilde{\gamma}_{O,N}] \quad (75a)$$

$$\Delta c_R = \frac{1}{nFD_R^{1/2}} \tilde{\gamma}_R(\Delta j_F) = \frac{1}{nFD_R^{1/2}} [\tilde{\gamma}_{R,1} + \tilde{\gamma}_{R,2} + \cdots + \tilde{\gamma}_{R,N}] \quad (75b)$$

Table 6
Partial Derivatives and Their Significance in Absolute Rate Theory (Butler-Volmer Behavior) under Nonequilibrium Conditions

Partial derivative	Shorthand notation	Meaning in ART (Butler-Volmer eqn.) ^a
$\delta j_F / \delta \phi$	$\tilde{F}$	$nFk_f[\alpha c'_O + (1 - \alpha)c'_R \exp \varphi] = \frac{RT}{nF} \frac{1}{R_{ct}}$
$\delta j_F / \delta c_O$	$\tilde{O}$	$-nFk_f$
$\delta j_F / \delta c_R$	$\tilde{R}$	$nFk_f \exp \varphi$
$\delta^2 j_F / \delta \phi^2$	$\tilde{FF}$	$-nFk_f[\alpha^2 c'_O - (1 - \alpha)^2 c'_R \exp \varphi - \alpha'(c'_O - c'_R \exp \varphi)]$
$\delta^2 j_F / \delta c_O \delta \phi$	$\tilde{OF}$	αnFk_f
$\delta^2 j_F / \delta c_R \delta \phi$	$\tilde{RF}$	$(1 - \alpha)nFk_f \exp \varphi$
$\delta^2 j_F / \delta c_O^2$	$\tilde{OO}$	0
$\delta^2 j_F / \delta c_R^2$	$\tilde{RR}$	0
$\delta^2 j_F / \delta c_O \delta c_R$	$\tilde{OR}$	0

^a $\alpha = -d(\ln k_f)/d\phi$, $\alpha' = -d^2(\ln k_f)/d\phi^2$.

The nature of these operators depends on the chemical, geometrical, and hydrodynamic circumstances. If, as in Section 2.3, the most simple model of a stationary planar electrode without chemical complications is adopted, one has:⁽²⁸⁾

$$\tilde{\gamma}_{O,i} = -\tilde{\gamma}_{R,i} = \int_0^t \frac{\Delta j_{F,i}(t-u)}{(\pi u)^{1/2}} du \quad (76)$$

Using Eqs. (74) to (76), it is possible to split the right-hand side of Eq. (73) into the separate orders, which can be equated to the corresponding current contributions. So:

$$\text{1st order:} \quad \Delta j_{F,1} + \lambda \tilde{\gamma}_{O,1} = \tilde{F} \cdot \varepsilon \quad (77)$$

$$\text{2nd order:} \quad \Delta j_{F,2} + \lambda \tilde{\gamma}_{O,2} = \tilde{FF} \cdot \varepsilon^2/2 - \lambda' \tilde{\gamma}_{O,1} \cdot \varepsilon \quad (78)$$

(For the meaning of λ and λ' , see Table 7.) The three terms in $\tilde{OO}$, $\tilde{OR}$, and $\tilde{RR}$ of Eq. (73) are omitted here, because we assume only a linear kinetic mechanism.

Regarding Eq. (76), both Eqs. (77) and (78) are integral equations of the current, which are hoped to be soluble after specification of ε . Evidently, Eq. (77) must be solved first, since Eq. (78) contains $\tilde{\gamma}_{O,1}$.

4.3.2. Elaboration for Specified ε

Before being general, we will outline the further procedure for the most simple case that

$$\varepsilon = (nF/RT)E_m \sin \omega_m t$$

Table 7
Specification of Symbols

Symbol	Meaning	Meaning in ART (Butler-Volmer eqn.)	Symbol	Meaning
λ	$(\bar{R} D_R^{-1/2} - \bar{O} D_O^{-1/2})/nF$	$k_f D_O^{-1/2} [1 + \exp \zeta]$	$A_m^{(0)}$	$\frac{1}{4R'_{ct}} \frac{nF \lambda'}{RT \lambda} \frac{1}{p_m + 2}$
λ'	$(\bar{R} F D_R^{-1/2} - \bar{O} F D_O^{-1/2})/nF$ $(= \delta \lambda / \delta \varphi)$	$k_f D_O^{-1/2} [(1 - \alpha) \exp (\zeta) - \alpha]$	$A_m^{(2)}$	$\frac{1}{-A_m^{(0)}} \frac{nF \lambda'}{RT \lambda} \frac{1}{p_m}$
p_m	$(2 \omega_m)^{1/2} / \lambda$		$B_m^{(2)}$	$\frac{nF \lambda'}{RT \lambda} \frac{1}{2R'_{ct}} \frac{p_m}{p_m^2 + 2p_m + 2}$
p_{2m}	$(4 \omega_m)^{1/2} / \lambda$		A_H	$A_m^{(2)} + A_n^{(2)} (\omega_m \text{ and } \omega_n \text{ different frequencies})$
$p_H = p_{m+n}$	$2^{1/2} (\omega_m + \omega_n)^{1/2} / \lambda$		A_L	$A_m^{(2)} + A_n^{(2)}$
$p_L = p_{m-n}$	$2^{1/2} (\omega_m - \omega_n)^{1/2} / \lambda$		B_H	$B_m^{(2)} + B_n^{(2)}$
R_{ct}	$1/(\delta f_F / \delta E) = (RT/nF)/\bar{F}$	$\frac{RT}{n^2 F^2} \frac{1}{k_f} \frac{1}{\alpha c'_O + (1 - \alpha) c'_R \exp \phi}$	B_L	$B_m^{(2)} + B_n^{(2)}$
R'_{ct}	$1/(\delta^2 f_F / \delta E) = (RT/nF)^2 / \bar{F} \bar{F}$	$\frac{RT}{nF} \frac{1}{R'_{ct}} = \frac{2\alpha - 1}{R_{ct}} - (\alpha^2 - \alpha + \alpha')$ $\times (c'_O - c'_R \exp \varphi) \frac{n^2 F^2}{RT} k_f$		

Naturally, for this waveform the first-order—linear—response can be postulated to be of the form

$$\Delta j_{F,1} = (a_m^{(1)} \sin \omega_m t + b_m^{(1)} \cos \omega_m t) E_m \quad (79)$$

For this function the integral of Eq. (76) can be solved (see Appendix I) in order to eliminate $\tilde{\gamma}_{0,1}$ in Eq. (77) and then $a_m^{(1)}$ and $b_m^{(1)}$ are found by equating the coefficients of $\sin \omega_m t$ and $\cos \omega_m t$. Taking $p_m = (2\omega_m)^{1/2}/\lambda$ (see Table 7), the result is

$$\Delta j_{F,1} = \frac{(p_m^2 + p_m) \sin \omega_m t + p_m \cos \omega_m t}{R_{ct}(p_m^2 + 2p_m + 2)} E_m \quad (80)$$

$$\lambda \tilde{\gamma}_{0,1} = \frac{(p_m + 2) \sin \omega_m t - p_m \cos \omega_m t}{R_{ct}(p_m^2 + 2p_m + 2)} E_m \quad (81)$$

(see also Eq. (51); in fact $a_m^{(1)} \equiv Y'$ and $b_m^{(1)} \equiv Y''$).

The same procedure has to be followed to elaborate the second-order relationship. However, Eq. (78) contains ε^2 and $\varepsilon \cdot \tilde{\gamma}_{0,1}$ and thus terms in $\sin^2 \omega_m t$ and $\sin \omega_m t \cos \omega_m t$. In view of the trigonometric relations

$$2 \sin^2 \omega_m t = 1 - \cos 2\omega_m t \quad (82a)$$

$$2 \sin \omega_m t \cos \omega_m t = \sin 2\omega_m t \quad (82b)$$

it must be anticipated that

$$\Delta j_{F,2} = [a_m^{(0)} + a_m^{(2)} \sin 2\omega_m t + b_m^{(2)} \cos 2\omega_m t] E_m^2 \quad (83)$$

in order to solve the convolution integral in Eq. (76).

Writing Eq. (78) generally as

$$\Delta j_{F,2} + \lambda \tilde{\gamma}_{0,2} = [A_m^{(0)} + A_m^{(2)} \cos 2\omega_m t + B_m^{(2)} \sin 2\omega_m t] E_m^2 \quad (84)$$

with specifications of $A_m^{(0)}$, etc. as in Table 7, and $p_{2m} = (2.2\omega_m)^{1/2}/\lambda$ the final result for $\Delta j_{F,2}$ is

$$\begin{aligned} \Delta j_{F,2} = & [A_m^{(0)} \exp(\lambda^2 t) \operatorname{erfc}(\lambda t^{1/2})] E_m^2 + \{[(p_{2m}^2 + p_{2m}) B_m^{(2)} - p_{2m} A_m^{(2)}] \\ & \times \sin 2\omega_m t + [p_{2m} B_m^{(2)} + (p_{2m}^2 + p_{2m}) A_m^{(2)}] \cos 2\omega_m t\} \\ & \times \frac{E_m^2}{p_{2m}^2 + 2p_{2m} + 2} \end{aligned} \quad (85)$$

4.3.3. Discussion

The sinusoidal part of Eq. (85) represents the expression for the main contribution to the second harmonic current response, denoted as a vector sum of two components $a_m^{(2)} \sin 2\omega t$ and $b_m^{(2)} \cos 2\omega t$. The current amplitude is, therefore, equal to $[(a_m^{(2)})^2 + (b_m^{(2)})^2]^{1/2}$. The frequency dependence is exclusively enclosed in the parameters p_m and p_{2m} : $p_m = (2\omega)^{1/2}/\lambda$ and $p_{2m} =$

$p_m(2^{1/2})$. The potential dependence is more composite, since the parameters $\lambda, \lambda', R_{ct}, R'_{ct}$ are all functions of potential. Note that in the absolute rate theory R_{ct} and R'_{ct} are more complex when the system is d.c. nonreversible, while λ and λ' are the same, irrespective of the d.c. mode of mass transfer. Simplified relations for d.c. reversible behavior are easily derived (see Table 7). Note the close connection of $A_m^{(2)}$ and $B_m^{(2)}$ with the first-order admittance components [Eq. (80)]. Typical examples of the constituting components and the final current as a function of frequency and potential are given in Figures 23 to 25, for d.c. reversible behavior.

The nonsinusoidal part of Eq. (85) represents a “d.c. current” which is evidently added to the original “zero-order” d.c. current. The existence of such a rectification was discovered by Fournier,⁽⁷¹⁾ at the same time as the discovery of a similar effect in the d.c. potential in controlled-current electrolysis by Doss and Agarwal.⁽²²⁾ In fact, Eq. (85) gives only the second-order contribution, whereas contributions of higher even-order can also be expected

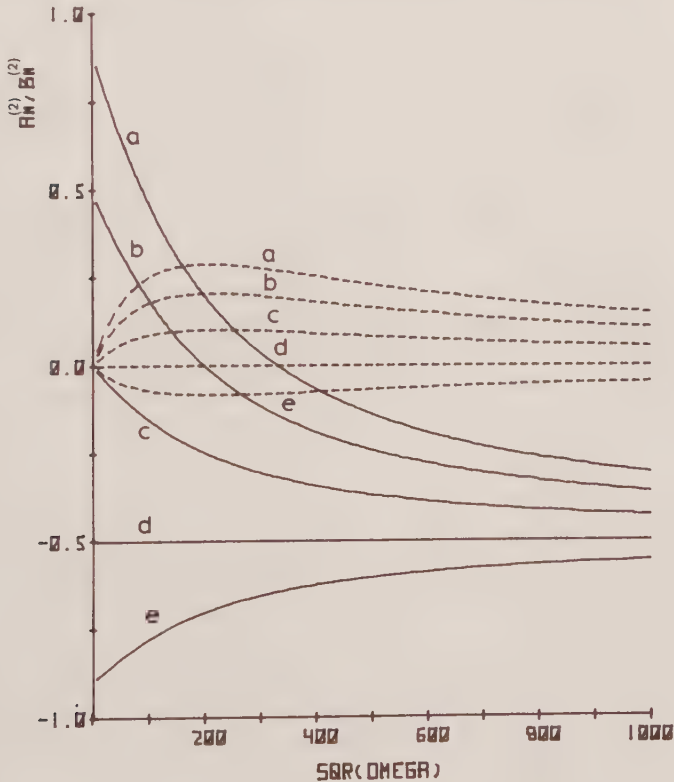


Figure 23. Frequency dependence of $A_m^{(2)} = -A_m^{(0)}$ (solid curves) and $B_m^{(2)}$ (dashed curves). Values of parameters chosen: $\alpha = 0.75, p_m = 0.01\omega^{1/2}; (nF/RT)/(4R_{ct}) = 1; 1/(4R'_{ct}) = (2\alpha - 1)/R_{ct}; 2(\lambda'/\lambda) =$ (a) -1.4 , (b) -1.0 , (c) -0.5 , (d) 0 , (e) 0.4 .

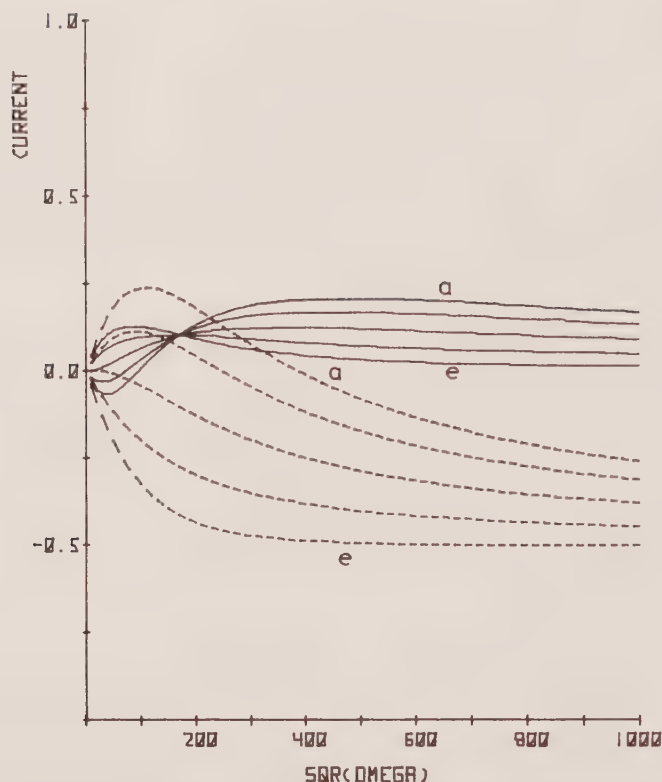


Figure 24. Frequency dependence of the sinus component $a_m^{(2)}$ (solid curves) and the cosinus component $b_m^{(2)}$ (dashed curves) in Eqs. (83) c.q. (85). Values of parameters chosen as in Figure 23.

at high amplitude excitations.⁽⁷²⁾ Plots of the whole rectification term are given in Figure 26.

4.3.4. Other Input Waveforms

Besides the second-harmonic and the rectification technique, some other methods are known, mainly for analytical purposes, which make use of additional properties of non-linear systems, such as modulation, intermodulation, and demodulation.

The input waveform in these techniques is either a sum or a product of sinusoidal functions with different frequencies. The theory can, however, be generalized by recalling that a product of two sine waves can always be decomposed according to

$$\begin{aligned} 2 \sin \omega_H t \sin \omega_L t &= \cos(\omega_H - \omega_L)t - \cos(\omega_H + \omega_L)t \\ &= \sin \omega_m t + \sin \omega_n t \end{aligned} \quad (86)$$

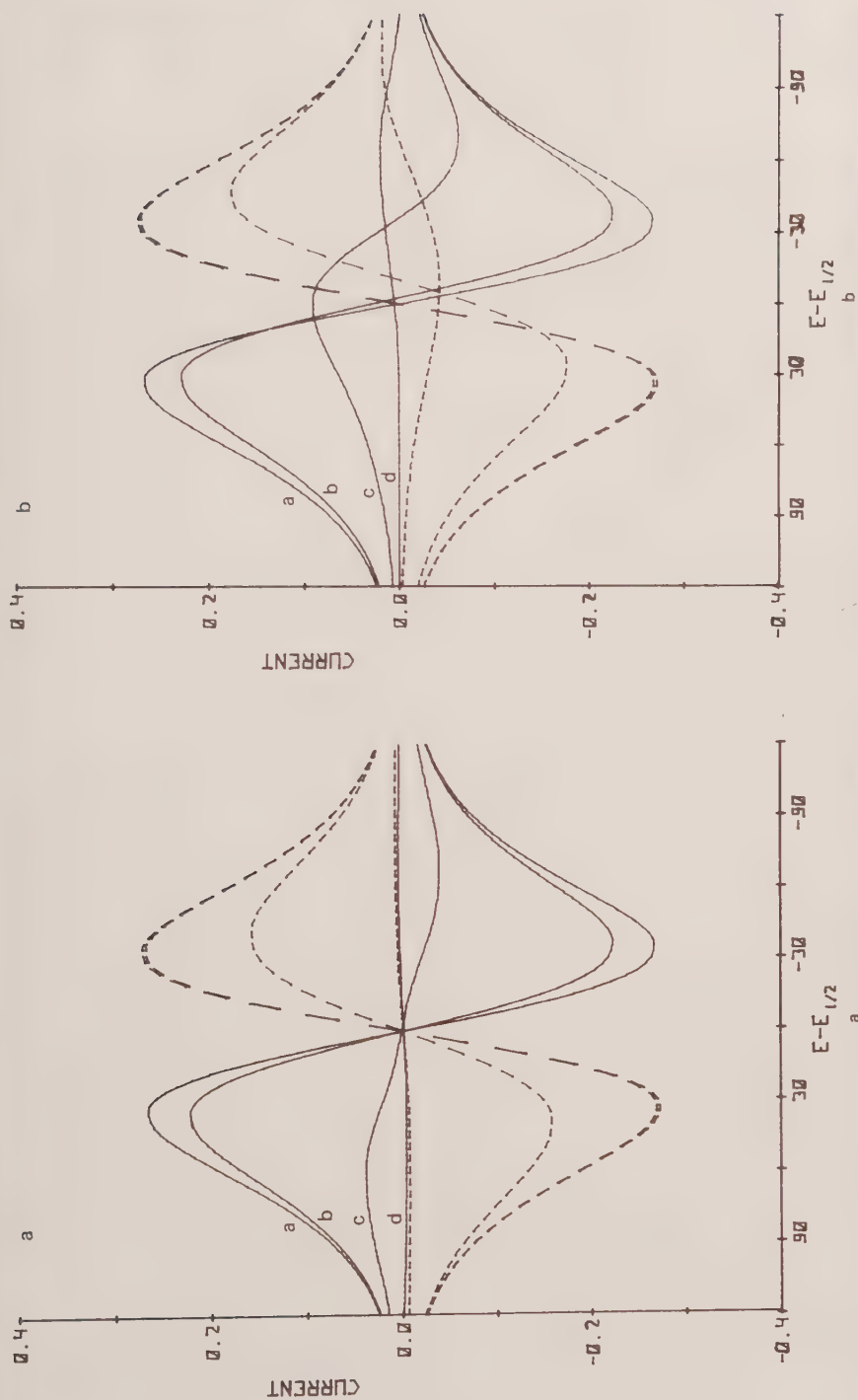


Figure 25. Potential dependence of the sinus component $a_m^{(2)}$ (solid curves) and the cosine component $b_m^{(2)}$ (dashed curves) in Eqs. (83) c.q. (85). Parameters chosen: $n = 1$; p_m at $E = E_{1/2}$: (a) 0.01, (b) 0.1, (c) 1, (d) 10; R_α at $E = E_{1/2}$: $R_\alpha = p_m$; values of α : 0.5 in Figure 25a and 0.75 in Figure 25b.

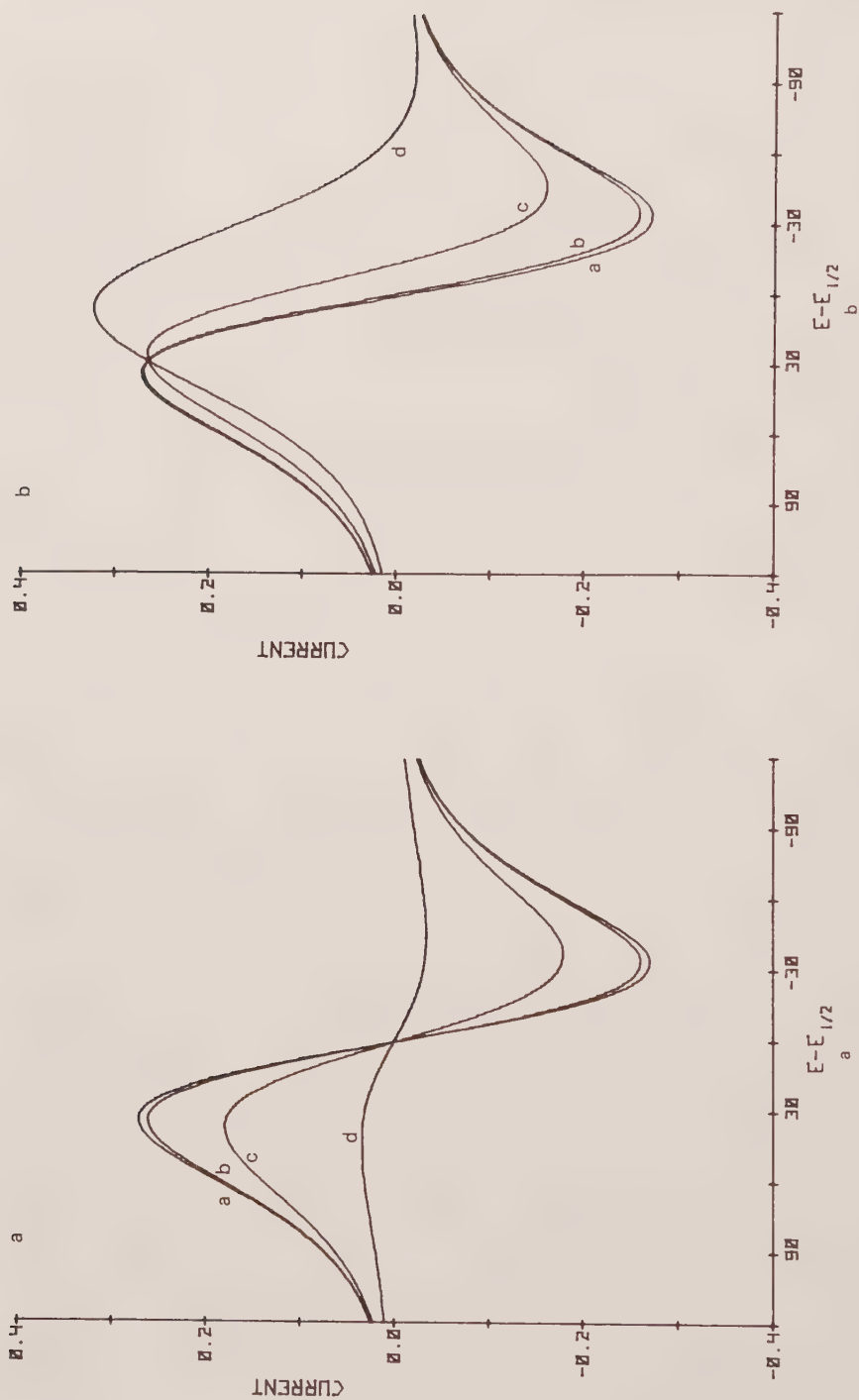


Figure 26. Potential dependence of the rectification component $a_m^{(0)}$ in Eqs. (83) c.q. (85). Parameters chosen as in Figure 25; values of α : 0.5 in Figure 26a and 0.75 in Figure 26b.

The input waveform can therefore be supposed to be of the form

$$\varepsilon = (nF/RT) \sum_{m=1}^N E_m \sin \omega_m t \quad (87)$$

with a maximum of $N = 3$ (regarding the techniques known at present).

The solution of the first-order integral equation (77) is straightforward, since each term in Eq. (87) gives rise to a response of the same frequency. So, $\Delta j_{F,1}$ and $\tilde{\gamma}_{0,1}$ will contain terms in ω_m , $\omega_n, \dots$, each given by expressions such as Eqs. (80) and (81).

In the second-order integral Eq. (78) the terms in ε^2 and $\varepsilon \cdot \tilde{\gamma}_{0,1}$ give rise to mixed products like $\sin \omega_m t \sin \omega_n t, \dots$, etc., as well as the products $\sin^2 \omega_m t$, $\sin^2 \omega_n t$, $\sin \omega_m t \cos \omega_n t, \dots$, etc., already discussed. Therefore, Eq. (84) has to be extended to a more general formula, that turns out to be

$$\begin{aligned} \Delta j_{F,2} + \lambda \tilde{\gamma}_{0,2} &= \sum_{m=1}^N [A_m^{(0)} + A_m^{(2)} \cos 2\omega_m t + B_m^{(2)} \sin 2\omega_m t] E_m^2 \\ &+ \sum_{m=1}^{N-1} \sum_{n=m+1}^N (A_m^{(2)} + A_n^{(2)}) [\cos (\omega_m + \omega_n)t - \cos (\omega_m - \omega_n)t] E_m E_n \\ &+ \sum_{m=1}^{N-1} \sum_{n=m+1}^N [(B_m^{(2)} + B_n^{(2)}) \sin (\omega_m + \omega_n)t \\ &- (B_m^{(2)} - B_n^{(2)}) \sin (\omega_m - \omega_n)t] E_m E_n \end{aligned} \quad (88)$$

The total expression for the current becomes:

$$\begin{aligned} \Delta j_{F,2} &= \sum_{m=1}^N [A_m^{(0)} \exp(\lambda^2 t) \operatorname{erfc}(\lambda t^{1/2})] E_m^2 \\ &+ \sum_{m=1}^N \frac{p_{2m}[(p_{2m} + 1)B_m^{(2)} - A_m^{(2)}] \sin 2\omega_m t + p_{2m}[B_m^{(2)} + (p_{2m} + 1)A_m^{(2)}] \cos 2\omega_m t}{p_{2m}^2 + 2p_{2m} + 2} E_m^2 \\ &+ \sum_{m=1}^{N-1} \sum_{n=m+1}^N \frac{p_H[(p_H + 1)B_H - A_H] \sin (\omega_m + \omega_n)t + p_H[B_H + (p_H + 1)A_H] \cos (\omega_m + \omega_n)t}{p_H^2 + 2p_H + 2} E_m E_n \\ &+ \sum_{m=1}^{N-1} \sum_{n=m+1}^N \frac{p_L[(p_L + 1)B_L - A_L] \sin (\omega_m - \omega_n)t + p_L[B_L + (p_L + 1)A_L] \cos (\omega_m - \omega_n)t}{p_L^2 + 2p_L + 2} E_m E_n \end{aligned} \quad (89)$$

where the meaning of $p_H = p_{m+n}$, $p_L = p_{m-n}$, B_H , B_L , A_H , and A_L is given in Table 7.

A survey of the different perturbation modes and the frequencies occurring in the current response is given in Table 8. The first mode mentioned is particular in this sense that only the amplitude of a single sine wave input is modulated by a time-dependent function $f(t)$. When it is supposed that this function varies slowly in time as compared to $\sin \omega_m t$, the derivation in Section 4.3.2. is still valid and leads to a current response with modulated amplitudes. The function $f(t)$ may be arbitrary, but well-known applications are a repetitive pulse, or a sinusoidal modulation $f(t) = 1 + E_L \sin \omega_L t$, where $\omega_L \ll \omega_H$. Detection of the current component with frequency ω_L essentially delivers the faradaic rectification component. On the other hand, this case may be considered as a limiting case of the fourth mode in Table 8, viz., for $\omega_L \ll \omega_H$ (or $\omega_m \approx \omega_n$).

4.3.5. Relation to Theories and Applications in Literature

The theory above is in agreement with the following more specific treatments in the literature:

- Matsuda and Delahay;⁽⁷³⁾ deriving the expression for the faradaic rectification current for a simple electrode reaction, $Ox + ne \rightleftharpoons Red$, obeying ART, and initially in equilibrium ($E_{dc} = E_{eq}$).
- McCord and Smith;⁽⁷⁴⁾ second-harmonic polarography for a similar electrode reaction, i.e., with d.c. polarization included and d.c. irreversible behavior admitted. (The expressions in this work are seemingly more complex, since they are in terms of current amplitude and phase angle, rather than in orthogonal components.) Moreover, highly elaborated extensions to cases of chemical reactions preceding or following charge transfer have been performed (see also Section 5).
- Zheletsov and Rafikov;⁽⁷⁵⁾ a.c. polarography using amplitude-modulated sinusoidal voltage ("demodulation polarography"), also for ART and nonreversible behavior. The expressions obtained by these authors are rather complex, probably because of the procedure employed (Fourier expansion) to arrive at relations between various coefficients.

An earlier treatment of demodulation polarography, presented by Brocke,⁽⁶⁷⁾ appears to be incorrect, as it considers the faradaic admittance as the j - E relation that is to be Taylor-expanded, thus ignoring that the admittance is only the first-order—linear—component of the non-linear absolute rate equation.

Because of the ART, the parameter α' does not occur in the formalisms mentioned, whereas in our treatment it simply arises as an operational parameter (which could be zero, of course).

Practical applications are mainly found in polarography with the analytical aim to reduce the background current due to the double layer capacity, which is less active in second-order behavior. Probably the earliest apparatus was

Table 8
Input Waveforms in Use in Second-order Techniques, Their Additive Components, and the Components Arising in the Resulting Current

Mode	Additive components	Components in second-order current			Detection on	Technique
$E_m f(t) \sin \omega_H t$	ω_H	$f t$	$2\omega_H$		$f(t)$	Faradaic rectification
$E_m \sin \omega_m t + E_n \sin \omega_n t$	ω_m	$f t$	$2\omega_m$	$\omega_m - \omega_n$	$\omega_m - \omega_n$	Intermodulation Demodulation
$E_H E_L \sin \omega_H t \sin \omega_L t$	$\omega_H - \omega_L$	$f t$	$2(\omega_H - \omega_L)$	$2(\omega_H + \omega_L)$	$2\omega_L$	
$E_H \sin \omega_H t (1 + E_L \sin \omega_L t)$	ω_H	$f t$	$2\omega_H$	$2(\omega_H - \omega_L)$	ω_L	Demodulation
			$2\omega_H$	$2(\omega_H + \omega_L)$	$2\omega_L$	

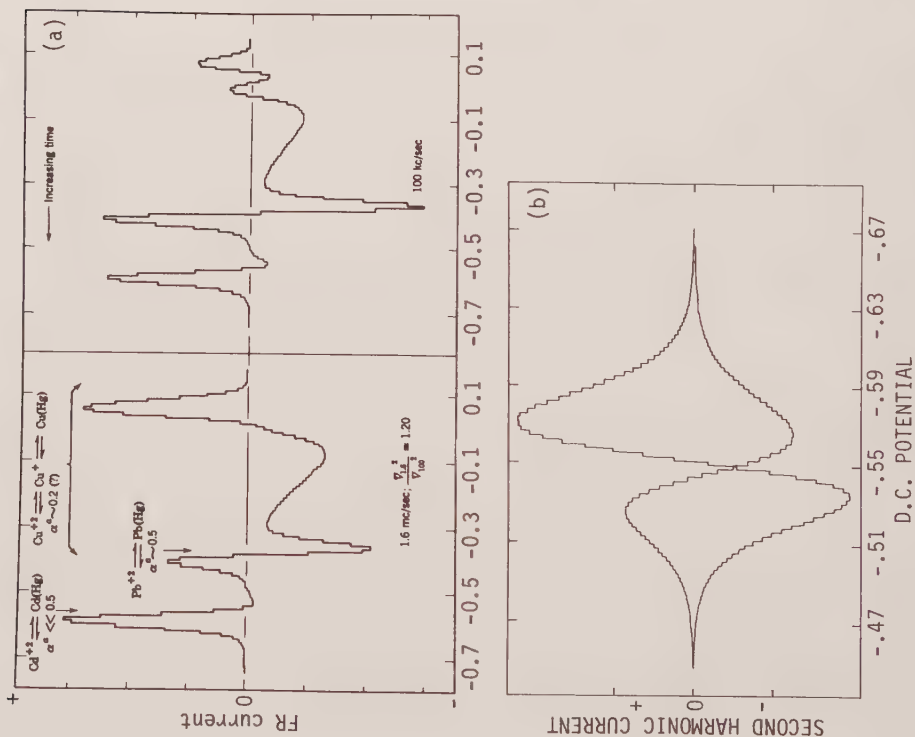


Figure 27. (a) Faradaic rectification polarogram of Cu^{2+} , Pb^{2+} and Cd^{2+} .⁽⁷⁷⁾ (b) Phase-sensitive second-harmonic polarogram of Cd^{2+} .⁽⁸⁰⁾ (c) Intermodulation polarograms of Tl^+ , Cd^{2+} and In^{3+} .⁽⁸¹⁾ The different shapes result from different combinations of the two frequencies.

the "radio-frequency polarograph", constructed by Barker,⁽⁷⁶⁾ employing the rectification effect, which could be detected as the square-wave current response to a square-wave modulated sinusoidal current of high frequency (100 KHz). Other applications are indicated in Table 8. Typical examples of results are represented in Figure 27.

Besides the analytical merits demonstrated, it appears to be rarely recognized that these techniques are valuable also for fundamental work, provided that double layer influences are properly accounted for. Significant applications are known from Barker^(77,78) (far. rect) and McCord⁽⁷⁹⁾ (sec. harm).

In this connection the question may arise, what is the best technique to choose, from theoretical and practical points of view. The answer is difficult to give, but some remarks are possible:

- The rectification principle allows working at very high frequency without much trouble, since the modulating signal (pulse, or square or sine wave) can be given a low frequency. Thus, predominance of the ohmic resistance is circumvented.
- This holds also for the intermodulation principle: when two high frequencies are applied, the detection frequency, $f_2 - f_1$, is low. However, it is difficult to measure the amplitude of the two input signals of so close frequency.
- When intermodulation is performed at low frequencies, f_1 and f_2 , serious interference may occur from other components of the response spectrum, e.g., $2f_1 - f_2$, etc. This accentuates the profit in second-harmonic measurements where, with modern electronics, locking to the double frequency may be very accurate.

Although numerous special features ("tricks") are imaginable, the instrumental set-up will generally consist of (a) the proper a.c. voltage source, (b) the potentiostat, (c) the cell, (d) the detector (see also Figure 21). Mostly it is essential to insert passive filters, which eliminate unwanted frequency components of high amplitude, in order to avoid the modulation of these components, intermodulation, rectification, or doubling in the detecting device itself. Detailed descriptions can be found in Reference (63).

4.4. A.C. Current Control

In the (perhaps hypothetical) case that it can be assumed that the *a.c. current* conducted through the interface by the faradaic reaction is forced to consist of only a zero-order (d.c.) and a first-order (fundamental a.c.) component, it follows from Eqs. (74) and (75) that Δc_O and Δc_R are also merely of first order. However, to examine the constitution of the resulting voltage response, it would be necessary to expand $\varepsilon = (nF/RT)\Delta E$ in terms of Δj_F and the Δc 's. When it is not possible to invoke relations like those in Table

5 (equilibrium situation), this leads to difficulties, because of the implicit nature of the rate equation. Solutions for this problem were discussed by Gellings,⁽⁸²⁾ applying Lagrange's inversion theorem, and by Rangarajan,⁽⁸³⁾ applying an operator formalism similar to that for the potential controlled case.

4.4.1. Expansion

We follow the approach of Rangarajan with the difference that we consider the d.c. conditions as a "pseudo-stationary state" on which the small amplitude perturbations are superimposed (i.e., the mean surface concentrations are "known" as a function of d.c. potential). Writing ε as a series of increasing order:

$$\varepsilon = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \dots \quad (90)$$

it can be stated that terms in ε_1 are first order, terms in ε_2 , ε_1^2 , and $\varepsilon_1 \Delta c$ are second order, and terms in ε_3 , $\varepsilon_1 \varepsilon_2$, and $\varepsilon_1^2 \Delta c$ are third order, etc. Thus it follows from Eq. (73) (Δj_F only first order) that:

$$\tilde{F} \cdot \varepsilon_1 = \Delta j_F - (\tilde{O} \cdot \Delta c_O + \tilde{R} \cdot \Delta c_R) = \Delta j_F + \lambda \tilde{\gamma}_O \quad (91)$$

$$\begin{aligned} \tilde{F} \cdot \varepsilon_2 = & -(\tilde{F}\tilde{F}/2)\varepsilon_1^2 - (\tilde{O}\tilde{F} \cdot \Delta c_O + \tilde{R}\tilde{F} \cdot \Delta c_R)\varepsilon_1 \\ & - \frac{1}{2}[\widetilde{OO} \cdot \Delta c_O^2 + 2\widetilde{OR} \cdot \Delta c_O \Delta c_R + \widetilde{RR} \cdot \Delta c_R^2] \end{aligned} \quad (92a)$$

or

$$\begin{aligned} \tilde{F} \cdot \varepsilon_2 = & -(\tilde{F}\tilde{F}/2)\varepsilon_1^2 + \lambda' \tilde{\gamma}_O \varepsilon_1 \\ & - \frac{1}{2}[\widetilde{OO}/D_O - 2\widetilde{OR}/D_O^{1/2}D_R^{1/2} + \widetilde{RR}/D_R] \frac{\tilde{\gamma}_O^2}{n^2 F^2} \end{aligned} \quad (92b)$$

where $\tilde{\gamma}_O$ is given by Eq. (75) (only first order) and λ and λ' are the same as in Eqs. (77) and (78) (cf Table 7). N.B. The same result is obtained via an alternative, but more tedious way, viz. solving the quadratic equation (73) for ε , writing out series expansions for terms like $(1+x)^{1/2}$ and $(1+x)^{-1}$, and carefully selecting the second-order products [cf. Eq. (18)].

4.4.2. Elaboration

It is natural to specify the current perturbation in the most simple case as $\Delta j_F = j_m \sin \omega_m t$, but there is no harm in a specification like Eq. (80) which must lead to a simple expression for ε_1 to be inserted, viz. $\varepsilon_1 = (nF/RT)E_m \sin \omega_m t$. The difference will show up in a different result for the phase angle of the second harmonics response, which will be referred to the current in the former case and to the first-order potential response in the latter case. With the aid of Eqs. (91) and (92) both proposals are easily introduced and lead, for $\widetilde{OO} = \widetilde{OR} = \widetilde{RR} = 0$, to:

(a) with $\Delta j_F = j_m \sin \omega_m t$:

$$\begin{aligned} \frac{\tilde{F}^2 \cdot \varepsilon_2}{j_m^2} = & -\frac{\widetilde{FF}}{4\tilde{F}} \frac{p_m^2 + 2p_m + 2}{p_m^2} + \frac{\lambda'}{\lambda} \frac{p_m + 2}{2p_m^2} \\ & + \left[\frac{\widetilde{FF}}{2\tilde{F}} \frac{p_m + 1}{p_m^2} - \frac{\lambda'}{\lambda} \frac{p_m + 2}{2p_m^2} \right] \sin 2\omega_m t \\ & + \left[\frac{\widetilde{FF}}{2\tilde{F}} \frac{p_m + 2}{2p_m} - \frac{\lambda'}{\lambda} \frac{1}{2p_m} \right] \cos 2\omega_m t \end{aligned} \quad (93)$$

(b) with $\varepsilon_1 = (nF/RT)E_m \sin \omega_m t$:

$$\begin{aligned} \frac{\tilde{F} \cdot \varepsilon_2}{E_m^2} = & - \left\{ \left(\frac{nF}{RT} \right)^2 \frac{\widetilde{FF}}{4} - \frac{nF}{RT} \frac{\lambda'}{\lambda} \frac{1}{2R_{ct}} \frac{p_m + 2}{p_m^2 + 2p_m + 2} \right\} [1 - \cos 2\omega_m t] \\ & - \frac{nF}{RT} \frac{\lambda'}{\lambda} \frac{1}{2R_{ct}} \frac{p_m}{p_m^2 + 2p_m + 2} \sin 2\omega_m t \end{aligned} \quad (94a)$$

$$= -[A_m^{(0)} + A_m^{(2)} \cos 2\omega_m t + B_m^{(2)} \sin 2\omega_m t] \quad (94b)$$

(See Table 7.)

4.4.3. Discussion

Comparison of Eq. (94) with Eq. (84) reveals the close connection between the potentiostatic and the galvanostatic approach. Evidently the current raised in the former is equal to the current that would flow if the system were subjected to a potential excursion of the same magnitude as obtained in the latter approach but of opposite polarity. This has been stated by Delahay *et al.*⁽¹¹⁾ in a general manner, which is similar to a comparison of Eqs. (92) and (78). The conclusion is that second-order potentiostatic and galvanostatic approaches are able to yield the same information about charge transfer kinetics. This information is implicated in the parameters $\tilde{F}$ (or R_{ct}), $\widetilde{FF}$ (or R'_{ct}), λ , and λ' , the other parameters (e.g., p_m , p_{2m}) being functions of these. As compared to the first-order impedance method (only $\tilde{F}$ or R_{ct} , and λ) this means an extension by two parameters, to be obtained by analysis of the frequency dispersion. As before (section 2.5), it is evident that interpretation of these parameters in terms of a model (e.g., ART) may be done via their potential dependence.

4.4.4. Faradaic Rectification

The only commonly known application of the galvanostatic approach is the measurement of the nonsinusoidal part of Eqs. (93) or (94), the faradaic rectification effect. It was discovered by Doss and Agarwal^(22,84) ("redoxokinetic effect"), and further developed by Delahay *et al.*⁽¹¹⁾ and by

Barker⁽⁷⁶⁾. The equations derived are easily identified with our more general expressions after introducing Butler–Volmer formulations. Apart from the extended information content, which was recognized much later,⁽²⁶⁾ the main advantage is that the perturbation signal can be of high frequency, whereas the response is measured at low frequency (essentially a d.c. signal, but usually detected as a periodic signal at the (low) frequency of the modulating waveform). This has the consequence that the restrictions caused by the ohmic resistance largely vanish.

The frequency limit is now set more trivially by the availability of power to generate a sufficiently large amplitude across the interface, since the ohmic resistance largely acts as a galvanostat resistor. Moreover this causes heating of the solution near the interface, so that the perturbation should be applied only during a short time (a few milliseconds).

Experimental set-ups for rectification measurements around the equilibrium potential (both *Ox* and *Red* present) have been designed by, among others, Delahay *et al.*,⁽¹¹⁾ de Leeuwe *et al.*,⁽⁸⁵⁾ and Agarwal.⁽⁸⁶⁾ A set-up with real potentiostatic control of the d.c. potential has been described by Van der Pol *et al.*⁽⁸⁷⁾

Typical examples of results are shown in Figures 28 and 29.

4.4.5. Data Analysis

Insight into the way to handle experimental results is most easily obtained by extracting the nonsinusoidal part of Eq. (94a) as $\Delta E_{\infty} = (RT/nF)\varepsilon_2$

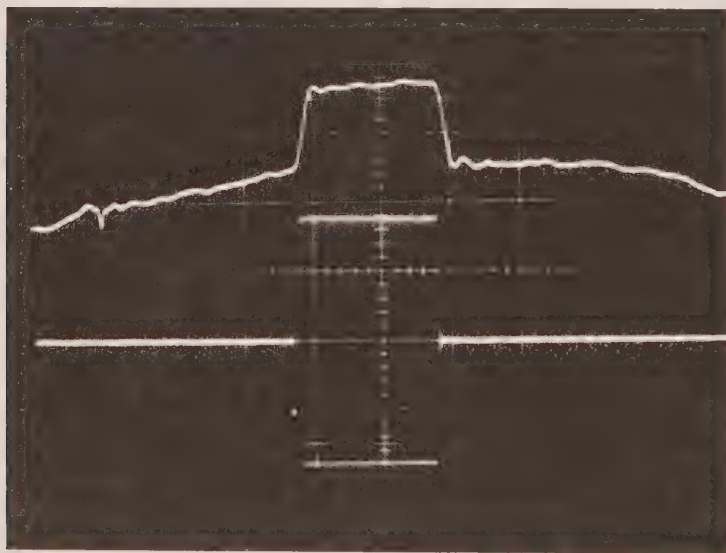


Figure 28. Typical oscilloscopic trace of the faradaic rectification voltage (upper trace) obtained from a pulse-modulated sine-wave current perturbation (lower trace).⁽⁸⁵⁾

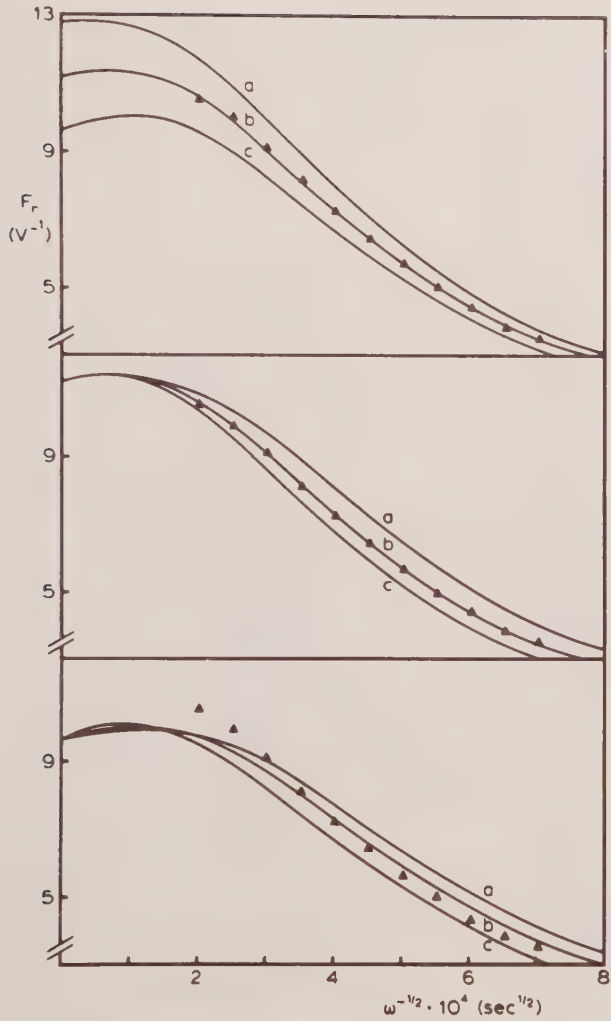


Figure 29. Frequency dependence of the faradaic rectification voltage response for the $\text{Cd}^{2+}/\text{Cd}(\text{Hg})$ electrode in 1 M KCl.⁽⁸⁵⁾ $F_r = \Delta E_\infty \cdot \omega^2 C_d^2$. The curves are theoretical plots for various combinations of $k_{sh} = k_f$ ($E = E^\circ$) and α : Upper Figure: $k_{sh} = 4$, cm s^{-1} , $\alpha = 0.79, 0.76, 0.73$; Middle Figure: $\alpha = 0.76$, $k_{sh} = 3, 4, 5 \text{ cm s}^{-1}$; Lower Figure: $\alpha = 0.73$, $k_{sh} = 3, 4, 5 \text{ cm s}^{-1}$.

(nonsinusoidal):

$$\frac{\Delta E_\infty}{E_m^2} = \frac{R_{ct}}{4R'_{ct}} - \frac{1}{2} \frac{nF}{RT} \frac{\lambda'}{\lambda} \frac{p_m + 2}{p_m^2 + 2p_m + 2} \tag{95}$$

Analysis of the right-hand side as a function of frequency is a three-parameter problem— R_{ct}/R'_{ct} , λ'/λ and $\lambda = (2\omega_m)^{1/2}/p_m$ —contrary to the statement above that four parameters are involved. However, E_m^2 in the left-hand side

contains the fourth parameter, as E_m^2 is related to the amplitude j_m of the controlled current by p_m and R_{ct} . Note that p_m pertains to the fundamental frequency ω_m (usually up to 10 MHz). Moreover there is a complication: the current forced through the cell is split up into a faradaic part Δj_F and a nonfaradaic part Δj_c due to the presence of the double layer capacity, C_d . Therefore, E_m^2 should be expressed in terms of the total current amplitude j_A by the function:

$$E_m^2 = \frac{j_A^2}{\omega^2 C_d^2} \frac{p_m^2 + 2p_m + 2}{(p_m + 1)^2 + (a_m + 1)^2} \quad (96)$$

with $a_m = p_m / \omega_m C_d R_{ct}$. This shows that both $C_d \cdot R_{ct}$ and C_d are additional parameters.

Several analysis procedures have been proposed,^(86,88) based on simplified expressions, that would be valid for high frequencies *casu quo* not too fast reactions, or the reverse. In fact, these are extrapolation procedures and, besides a large inaccuracy in the results, the danger of enormous systematic errors exists, when the assumed simplification is not permitted in reality.^(89,90) An example of this is shown in Figure 30. Many earlier published data may, therefore, be unreliable.

An interesting feature is that it is possible to create conditions to obtain a zero rectification effect: $\Delta E_\infty = 0$. This reduces Eq. (95) to one equation with two unknowns. If two such cases are created (e.g., at different d.c.

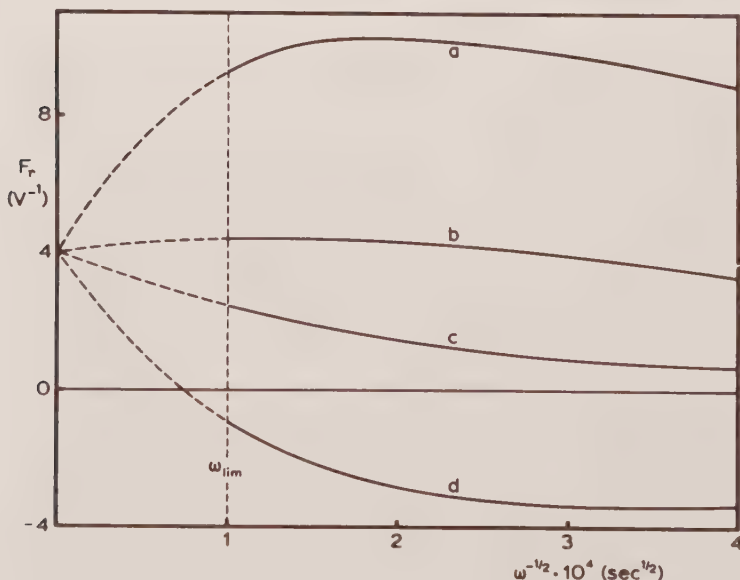


Figure 30. Calculated plots of $F_r = \Delta E_\infty \cdot \omega^2 C_d^2$ vs. $\omega^{-1/2}$, showing the impossibility of proper extrapolation to infinite frequency.⁽⁹⁰⁾ Parameters chosen: $R_{ct} \cdot \lambda = 30 \Omega \text{ cm}^2 \text{ s}^{-1/2}$, $k_{sh} = 8 \text{ cm s}^{-1}$, $\alpha = 0.6$, $n = 2$, $C_d = 30 \mu\text{F cm}^{-2}$; ratio of $c_O^* D_O^{1/2} / c_R^* D_R^{1/2}$: (a) 10.0, (b) 1.75, (c) 1.0, (d) 0.46.

potentials) it may be possible to determine the system parameters after a kinetic model has been adopted. Usually, however, a numerical analysis of Eq. (95) as a function of frequency, at different potentials, is preferable, because then the conditions can be chosen so as to yield maximal information about the desired parameters.⁽⁹⁰⁾

4.5. Second-order Behavior of the Double Layer

Thus far only faradaic non-linearity has been considered. However, the process of charging the double layer is in nature non-linear too, as there is a non-linear relation between the charge density q on the electrode and the interfacial potential E . Usually this is accounted for by assigning the first-order parameter $C_d = dq/dE$ and stating that C_d is potential-dependent. When we expand to higher orders we may have

$$\Delta q = \Delta q_1 + \Delta q_2 + \dots = C_d(\Delta E_1 + \Delta E_2 + \dots) + \frac{1}{2} \frac{dC_d}{dE} (\Delta E_1 + \Delta E_2 + \dots)^2 \quad (97)$$

Considering the two modes of control:

(a) a.c. potential control: $\Delta E_2 = 0$, so

$$\Delta j_{c,2} = \frac{d\Delta q_2}{dt} = \frac{1}{2} \frac{dC_d}{dE} \frac{d(\Delta E_1)^2}{dt} \quad (98)$$

(b) a.c. current control: $\Delta j_{c,2} = 0$, $\Delta q_2 = 0$, so:

$$C_d \Delta E_2 = -\frac{1}{2} \frac{dC_d}{dE} (\Delta E_1)^2 \quad (99)$$

where Δj_c denotes the capacity current and all ΔE 's denote the contributions of several orders to the *interfacial* potential.

Elaboration for $\Delta E_1 = E_m \sin \omega_m t$ reveals that the second-order current is purely second harmonic, while the second-order potential contains a rectification component in addition. Typical plots of the essential factors dC_d/dE and $(1/C_d)dC_d/dE$ are represented in Figure 31.

4.6. Behavior of the Total Cell

The simultaneous occurrence of the faradaic and the nonfaradaic non-linearity complicates the understanding of the behavior of the total cell, i.e., of what can be actually measured. The discussion may be illustrated with the aid of Figure 32.

In this schematic picture the cell is represented as a four-pole, having two connections to the excitation source (either galvanostatic or potentiostatic) and two others to the detection device, which has an input resistance R_D . Appropriate filters prevent the fundamental current from flowing through the detector circuit and the second-order current from flowing through the excitation circuit. These filters are hypothetically supposed to act ideally, with no

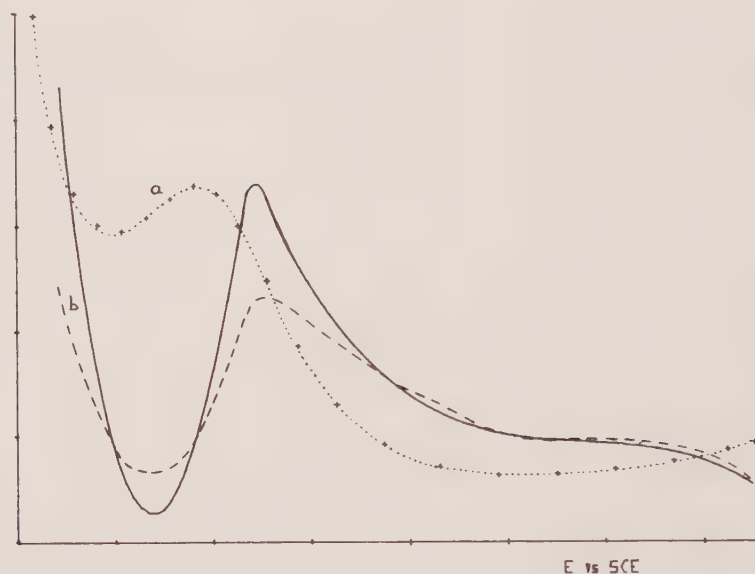


Figure 31. (a) Double layer capacity C_d as a function of potential at a mercury electrode in 1 M KCl⁽¹⁵⁾; (b) dC_d/dE (solid curve) and $(1/C_d)dC_d/dE$ (dashed curve).

substantial internal impedance. Our main concern will be the interfacial potential $\Delta E = \Delta E_1 + \Delta E_2 + \dots$ (the subscripts denote distinct orders).

4.6.1. First-order Interfacial Potential

Using the operational impedance concept (of Section 3.5), ΔE_1 produced by the excitation is readily expressed via its Laplace transform:

$$\Delta \bar{E}_1(s) = \bar{V}(s) - R_\Omega \bar{j}_1(s) = \frac{Z_F(s) \cdot Z_C(s)}{Z_F(s) + Z_C(s)} \bar{j}_1(s) \quad (100)$$

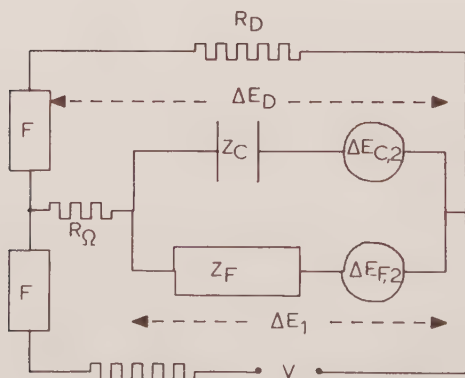


Figure 32. Hypothetical equivalent circuit of the cell connected to the source of excitation (V) and the input (R_D) of the measuring device. F , hypothetical filters; Z_F , faradaic impedance, Z_C , double layer impedance; $\Delta E_{F,2}$, $\Delta E_{C,2}$, hypothetical second-order voltage sources (generated).

When $Z_F(s)$, $Z_C(s)$, and $j_1(t)$ are specified, ΔE_1 can be obtained by deconvolution of the right-hand side of Eq. (100). In fact this has been done in Eq. (96) to obtain E_m^2 when $j_1 = j_A \sin \omega_m t$.

4.6.2. Second-order Interfacial Potential

The appearance of second-order effects is represented in Figure 32 by two hypothetical voltage sources with zero internal impedance, in the faradaic branch and the double layer branch, which merely "produce" second-order currents.⁽⁹¹⁾ These currents will flow through the detector circuit as though the constituting elements (including Z_F and Z_C) were linear again. That this model is permitted follows easily from the theory in sections 4.3, 4.4, and 4.5. Note that now the currents $j_{F,2}$ and $j_{C,2}$ are just the currents produced by *both* voltage sources and no longer equal to $\Delta j_{F,2}$ and $\Delta j_{C,2}$ in Sections 4.3 and 4.5.

Applying Kirchhoff's laws it can be derived that

$$\begin{aligned}\overline{\Delta E_2(s)} &= \overline{\Delta E_{F,2}(s)} - Z_F(s) \cdot \overline{j_{F,2}(s)} \\ &= \overline{\Delta E_{C,2}(s)} - Z_C(s) \cdot \overline{j_{C,2}(s)} \\ &= (R_\Omega + R_D)[\overline{j_{F,2}(s)} + \overline{j_{C,2}(s)}]\end{aligned}\quad (101)$$

from which we obtain the voltage across the detector input:

$$\begin{aligned}\frac{\overline{\Delta E_D(s)}}{R_D} &= \frac{\overline{\Delta E_2(s)}}{R_\Omega + R_D} = \overline{j_{F,2}(s)} + \overline{j_{C,2}(s)} \\ &= \frac{Z_F(s)Z_C(s)}{Z_F(s)Z_C(s) + (R_\Omega + R_D)[Z_F(s) + Z_C(s)]} \left[\frac{\overline{\Delta E_{F,2}(s)}}{Z_F(s)} + \frac{\overline{\Delta E_{C,2}(s)}}{Z_C(s)} \right]\end{aligned}\quad (102)$$

and the limiting cases:

$$(a) \quad R_\Omega + R_D \rightarrow 0: \quad \frac{\overline{\Delta E_D(s)}}{R_D} \rightarrow \frac{\overline{\Delta E_{F,2}(s)}}{Z_F(s)} + \frac{\overline{\Delta E_{C,2}(s)}}{Z_C(s)} = \overline{\Delta j_{F,2}(s)} + \overline{\Delta j_{C,2}(s)} \quad (103)$$

$$\begin{aligned}(b) \quad R_D \rightarrow \infty: \quad \Delta E_D(s) &\rightarrow \left[\frac{1}{Z_F(s)} + \frac{1}{Z_C(s)} \right]^{-1} \\ &\times \left\{ \frac{\overline{\Delta E_{F,2}(s)}}{Z_F(s)} + \frac{\overline{\Delta E_{C,2}(s)}}{Z_C(s)} \right\} = \overline{\Delta E_2(s)}\end{aligned}\quad (104)$$

In the latter case (galvanostatic) the two voltage sources are competing in building up the interfacial potential. This is the reason why, for example, the faradaic rectification voltage cannot be measured immediately after the start of the a.c. electrolysis,⁽¹¹⁾ but after a certain time delay in which the double layer is being charged.

5. Special Applications to More Involved Systems

5.1. Introduction

The theory of the impedance in Section 2 has been focused to a fairly simple model of the electrode process (single electron transfer + diffusion and separate parallel double layer charging) for two reasons: (a) it is the most commonly treated model, also in methodologies of other small-amplitude relaxation methods; (b) it is most suitable to demonstrate the use of impedance measurements as a function of both the frequency and the d.c. potential. However, because of the relative simplicity of relational expressions in the frequency domain, the impedance method is especially useful for adaptation to more complex models which possibly may represent an experimental situation more exactly (one may even wonder whether any real example of simple behavior exists). It would be impossible within the scope of this chapter to reproduce all of the more sophisticated treatments that exist in the literature nowadays. We therefore selected for this section some examples suitable to outline a certain principle for which many variations are feasible.

Although our more implicit treatment of the theory of second-order phenomena in Section 4 suggests otherwise, explicit applications to models other than the simple one (called "Randles behavior") are scarce in the literature. At present this appears to be an omission, since the fundamental extension of information provided should make the second-order methods most promising, especially for more complex behavior. Nevertheless we necessarily confine ourselves mainly to first-order theory, but we owe to Section 4 the more philosophical formulation of the impedance concept, as follows:

- First-order expansion of the faradaic current as

$$\Delta j_F = \frac{\partial j_F}{\partial \varphi} \varepsilon + \sum_{i=2}^N \frac{\partial j_F}{\partial c_i} \Delta c_i \quad (105)$$

where the summation concerns all species involved in the actual charge transfer process.

- Elimination of the Δc 's by appropriate operators on j_F :

$$\Delta c_i = \frac{1}{nFD_i^{1/2}} \tilde{\gamma}_i \quad (106)$$

leading to

$$\Delta j_F + \sum_{i=2}^N \lambda_i \tilde{\gamma}_i = \tilde{F} \varepsilon = \frac{nF}{RT} \tilde{F} \Delta E \quad (107)$$

where $\tilde{F} = \partial j_F / \partial \varphi$ and $\lambda_i = -(nFD_i^{1/2})^{-1} \partial j_F / \partial c_i$.

- Laplace transformation of Eq. (107) with $s = i\omega$:

$$\mathcal{L} \Delta j_F(i\omega) + \sum_{i=2}^N \lambda_i \mathcal{L} \tilde{\gamma}_i(i\omega) = \frac{nF}{RT} \tilde{F} \mathcal{L} \Delta E(i\omega) \quad (108)$$

from which either the faradaic impedance or admittance can be derived.

- A similar treatment of the double layer charging:

$$\Delta j_c = d\Delta q/dt \quad (109)$$

or

$$\mathcal{L}\Delta j_c(i\omega) = i\omega\mathcal{L}\Delta q(i\omega) \quad (110)$$

$$\Delta q = \left(\frac{\partial q}{\partial E}\right)_{\Gamma_i} \Delta E + \sum_{i=0}^N \left(\frac{\partial q}{\partial \Gamma_i}\right)_E \Delta \Gamma_i \quad (111)$$

where the summation concerns all species whose surface excesses can be varied independent of E . For further discussion, see Section 5.4.

5.2. Randles Behavior

Looking back to the treatment in Section 2, but now with regard to Eqs. (105) through (111), it appears that a more general characterization of Randles behavior could be formalized as:

$$(a) \quad \mathcal{L}\tilde{\gamma}_i(s) = \pm s^{-1/2} \mathcal{L}\Delta j_F(s) \quad (112)$$

$$(b) \quad \Delta q = C_d \Delta E \quad (113)$$

(i.e., all surface excesses are only dependent on E). In Eq. (112), the + sign pertains to *Ox* species, the – sign to *Red* species.

Clearly this formalism always results in the equivalent circuit of Figure 3a, the elements in it being defined by

$$R_{ct} = (RT/nF)\tilde{F}^{-1} \quad (114a)$$

$$\sigma = R_{ct} \sum_{i=2}^N \pm \lambda_i / 2^{1/2} = R_{ct} \lambda / 2^{1/2} \quad (114b)$$

$$C_d = dq/dE \quad (114c)$$

The difference with respect to the premises in Section 2 is that nothing is specified about the model determining the parameters λ_i and $\tilde{F}$ (and perhaps even C_d). In Eq. (114b), the plus sign pertains to oxidized species.

In view of this philosophy, some further remarks can be made concerning special phenomena obeying “Randles behavior.”

(i) *Stoichiometry*. The overall reaction does not need to be first-order in only two species O and R , but may be of the general type



Then the transfer of n electrons is related to the flux of ν_i^* particles of species i . This is in the theory most easily accounted for by a new definition of λ_i :

$$\lambda_i = -\nu_i^* (nFD_i^{1/2})^{-1} \partial j_F / \partial c_i \quad (115)$$

to be introduced into Eq. (107). Remembering Reinmuth's considerations,⁽²⁶⁾ cf. Section 4.2, it can be deduced that, for small departures from the *equilibrium*

situation, the thermodynamic relationships are generally of the type

$$\partial j_F / \partial c_i = \pm (\nu_i^* / c_i^*) \tilde{F} \quad (116)$$

so that eventually the Warburg coefficient for species i is proportional to $(\nu_i^*)^2 / n^2$.

Apart from this macroscopic picture, one must distinguish the microscopic stoichiometry, that is the manner of involvement of species in the actual charge transfer across the interface. The simultaneous collision of all the particles in the overall scheme being improbable, it is often assumed that charge transfer occurs via several steps, involving intermediate states. The stoichiometry in these partial processes, together with the extent to which they are rate-determining, determines the explicit nature of the partial derivatives $\partial j_F / \partial c_i$ and $\partial j_F / \partial \varphi$, i.e., of λ_i and $\tilde{F}$. As a consequence the microscopic stoichiometric coefficients $\nu_O, \nu_R \dots \nu_i$ play their role in addition to k_f and α already introduced in Section 2. Note that ν_i is not necessarily equal to ν_i^* and also not necessarily an integer.⁽²⁶⁾ Some examples are given in Table 9 (see next section).

(ii) *Negative faradaic impedance.* The major cause of the potential dependency of the rate constants is the effect of the interfacial potential itself, causing k_f to decrease and $k_b = k_f \exp(\varphi)$ to increase with increasing E . Consequently one has $0 < \alpha < 1$. However, if additional potential-dependent effects are significant, this is not necessarily so. The most illustrative example is the acceleration or inhibition of charge transfer by adsorbed species. When this adsorption is strongly potential-dependent, its effect on k_f and k_b may make $\alpha > 1$ or, conversely, $\alpha < 0$. The result is that in the *non-d.c. reversible case*, where α appears directly in the expression for R_{ct} and σ [see Eqs. (29), (32), and (33)], the *total* faradaic impedance may become negative.^(92,93) An example is reproduced in Figure 33.

(iii) *Parallel processes.* Assuming that mutual interaction is absent, the occurrence of two or more charge transfer processes can be treated by separate elaboration of Eq. (107) for each process. Because of the additivity of the corresponding currents, the admittance representation is most favorable. In other words, the admittances for each process are connected in parallel in the equivalent circuit. The analysis of the overall admittance (obtained experimentally) is not always unambiguous, as is shown in Figure 34.⁽⁹⁴⁾

(iv) *Series processes.* Obviously the impedance of any practical electrochemical cell is made up of the sum of the ohmic resistance and the two interfacial impedances belonging to the two terminals. Often one of these impedances is made negligible by choosing the surface area of one electrode large as compared to that of the electrode of interest. If this is not possible, the composite impedance should be considered. The latter is relevant especially in studies of solid electrolytes⁽⁹⁵⁾ and of membranes placed in between nonidentical solutions.⁽⁹⁶⁾ Typical examples of equivalent circuits resembling Randles behavior (at least in a certain frequency region) are shown in Figure 35.

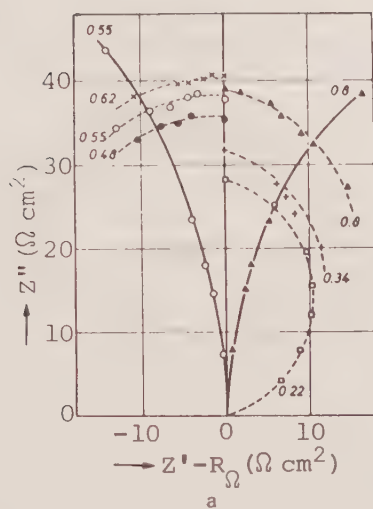
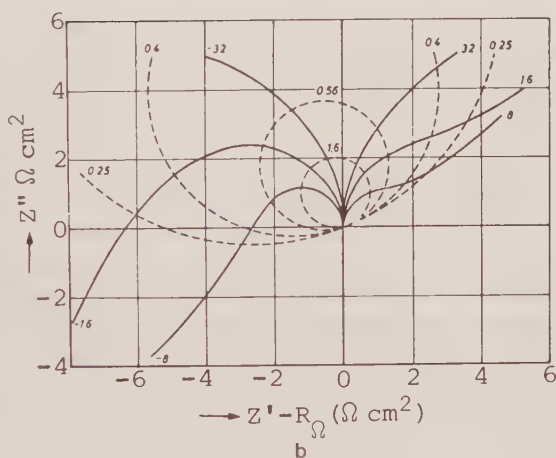


Figure 33. Impedance plane diagrams for positive and negative faradaic impedance, with variation of frequency (solid curves) and variation of concentration (dashed curves). (a) Experimental (dropping mercury electrode) for the oxalato-Fe(III)/Fe(II) electrode reaction in $0.2\text{ M Na}_2\text{Ox} + 0.05\text{ M H}_2\text{Ox} + 0.06 \times 10^{-3}\text{ M}$ sodium dodecylsulfate; frequency variation plots obtained at -0.08 and -0.55 V vs. SCE and 0.02 M Fe(III) ; concentration variation plots at 420 Hz and the potentials indicated. (b) Theoretical for fixed Cd ($20\text{ }\mu\text{F cm}^{-2}$) and R_{ct}/σ ratio ($p' = 0.08$); numbers of R_{ct} indicated in $\Omega\text{ cm}^{-2}$ and frequencies (dashed curves) in kHz .⁽⁹²⁾



(v) *Pseudo-Randles behavior*. Clearly the Randles circuit corresponds to a specific frequency dispersion function, which is entirely defined by two “time constants”, i.e., $R_{ct}C_d$ (dimension s^{-1}) and λ (dimension $\text{s}^{-1/2}$). However, when a set of experimental data can be fitted to this function, it cannot unambiguously be concluded that Randles behavior prevails. In fact, several limiting cases of the more complex circuits to be treated in the following, fit to the same function, but with a different significance of the time constants. In the literature this behavior is qualified as “pseudo-Randles behavior,” i.e., it is possible to determine values for a “charge transfer resistance,” a “Warburg coefficient,” and a “parallel capacity,” but these values fail to obey all of the definitions in Eq. (114).

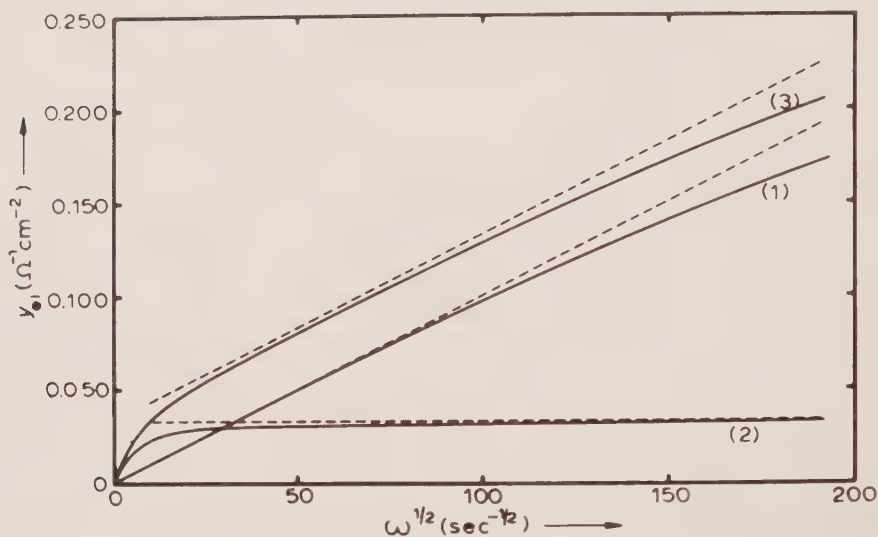


Figure 34. Theoretical plots of the in-phase component of the interfacial admittance in the case of two parallel electrode reactions (1) and (2), characterized by $R_{ct}(1) = 1.5 \Omega \text{ cm}^2$, $p'(1) = 3 \times 10^{-3}$, and $R_{ct}(2) = 30 \Omega \text{ cm}^2$, $p'(2) = 3 \times 10^{-1}$. Curves (1) and (2): Y' for the separate reactions; curve (3): sum of (1) and (2). The broken lines show the divergence from straight lines.⁽⁹⁴⁾

5.3. Multiple Step Charge Transfer

When a charge transfer process involves more than one electron it could be supposed that there is *one* transition state involving the total charge to be transferred, which leads to classical rate equations like Eq. (10). On the other hand reactions proceeding via two or more transition states are likely as well. The reaction mechanism is then split into steps involving intermediate species with descending oxidation states from *O* to *R*. The cases to be treated below have been limited to two-step mechanisms for the sake of simplicity, but can easily be generalized to more steps. It is questionable, however, whether present analysis procedures are suited for establishing very complex schemes unambiguously.

5.3.1. Unstable Intermediate

In a two-step scheme, the intermediate *Y* is involved in two redox-couples, viz. (1) *O*/*Y* and (2) *Y*/*R*. In the presence of *O*, the concentration of *Y* is negligibly small if $E \gg E_1^\circ$, and similarly in the presence of *R* if $E \ll E_2^\circ$. Consequently, if $E_1^\circ \ll E_2^\circ$ ("reversed standard potentials") the interfacial concentration c_Y is negligibly small during charge transfer *at any potential*. Therefore, no substantial diffusional or other type of mass transfer of *Y* occurs, so that the velocities of the partial steps v_1 and v_2 must be equal. With this condition, $v_1 = v_2$, c_Y can be eliminated from the partial rate equations,

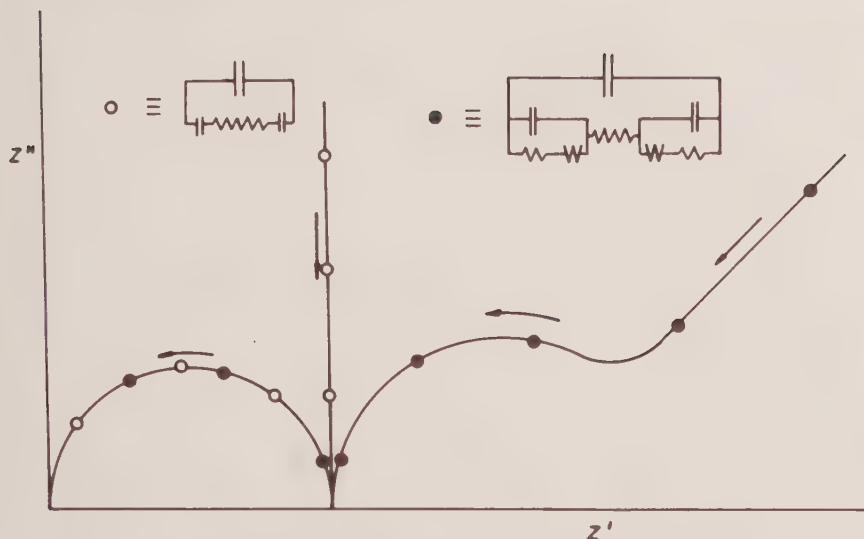


Figure 35. Predicted shape of complex impedance plot of a thin layer cell with identical electrodes, taking account of the geometrical capacity. (○) no electrode reaction ("polarized" or "blocking" electrodes), (●) with electrode reaction, controlled by charge transfer and diffusion.⁽⁹⁵⁾

leading to an "overall" rate equation for charge transfer, involving only c_O and c_R . Depending on the type of mechanism, the microscopic stoichiometry—and thus the specification of $\tilde{F}$ and λ_i —are more or less complex. The mass transfer operators $\tilde{\gamma}_O$ and $\tilde{\gamma}_R$, however, are independent of the mechanism, as the fluxes of O and R are only related to the overall current. So, when mass transfer is controlled solely by diffusion, *real* Randles behavior always prevails, and only $\tilde{F}$ and λ imply the mechanism. Some typical examples (probably the most simple ones) are compiled in Table 9.^(12,97)

5.3.2. Solution-soluble Intermediate

We shall consider the mechanism⁽⁹⁸⁾



where now Y may be present in a substantial concentration and may thus be transported by diffusion. Therefore we have

$$v_1 = f(c_O, c_Y, E) \quad (117a)$$

$$v_2 = f(c_Y, c_R, E) \quad (117b)$$

$$-\Delta j_F = n_1 F \Delta v_1 + n_2 F \Delta v_2 \quad (118)$$

$$\overline{\Delta c_O}(s) = -D_O^{-1/2} s^{1/2} \overline{\Delta v_1}(s) \quad (119a)$$

$$\overline{\Delta c_R}(s) = D_R^{-1/2} s^{-1/2} \overline{\Delta v_2}(s) \quad (119b)$$

$$\overline{\Delta c_Y}(s) = D_Y^{-1/2} s^{-1/2} [\overline{\Delta v_1}(s) - \overline{\Delta v_2}(s)] \quad (119c)$$

This set of equations is sufficient to derive, via Taylor expansion of v_1 and v_2 and elimination of the unknown partial currents $n_1 F \Delta v_1$ and $n_2 F \Delta v_2$, an expression for the operational admittance as specified in Table 10. This expression is identical to that of Armstrong and Firman,⁽⁹⁸⁾ though the notations and the arrangements are different.

Table 9

Some examples of D.C. Reversible Two-step Electrode Reactions with Unstable Intermediate, with Resulting Expressions for the Potential Dependence of $\lambda = \sigma\sqrt{2}/R_{ct}$

Mechanism	Rate equation: $-j_F/2F =$	Potential dependence of k_f and $\lambda = \lambda_O - \lambda_R$
$O + e \rightleftharpoons Y \quad (R_1)$ $Y + e \rightleftharpoons R \quad (R_2)$	$k_f[c_O - c_R \exp(\varphi)]$	$\frac{1}{k_f} = \frac{1}{k_1} + \frac{K_1}{k_2}$ $= \frac{\exp(\frac{1}{2}\alpha_1\varphi)}{k_{s1}} + \frac{\exp[\frac{1}{2}(1+\alpha_2)\varphi]}{k_{s2}}$ $\lambda = (k_f/D_O^{1/2})[1 + \exp(\zeta)]$
$O + e \rightleftharpoons Y \quad (R_1)$ $2Y \rightleftharpoons O + R \quad (R_d)$ R_1 rate-determining	$k_f[c_O - c_O^{1/2}c_R^{1/2} \exp(\frac{1}{2}\varphi)]$	$\frac{1}{k_f} = \frac{1}{k_1} = \frac{\exp(\frac{1}{2}\alpha_1\varphi)}{k_{s1}}$ $\lambda = \frac{1}{2}(k_f/D_O^{1/2})[1 + \exp(\zeta)]$
<i>idem</i> , R_d rate-determining	$k_f[c_O^2 - c_Oc_R \exp(\varphi)]$	$\frac{1}{k_f} = \frac{K_1^2}{K_d k_d} = \frac{\exp(\varphi)}{K_d k_d}$ $\lambda = (k_f/D_R^{1/2})c_O^* \exp(-\varphi)$
$2O + 2e \rightleftharpoons Y \quad (R_1)$ $Y \rightleftharpoons O + R \quad (R_d)$	$k_f[c_O^2 - c_Oc_R \exp(\varphi)]$	$\frac{1}{k_f} = \frac{1}{k_1} + \frac{K_1}{k_d}$ $= \frac{\exp(\alpha_1\varphi)}{k_{s1}} + \frac{\exp(\varphi)}{K_d k_d}$ $\lambda = (k_f/D_R^{1/2})c_O^* \exp(-\varphi)$
$O + R \rightleftharpoons Y \quad (R_r)$ $Y + 2e \rightleftharpoons 2R \quad (R_2)$	$k_f[c_Oc_R - c_R^2 \exp(\varphi)]$	$\frac{1}{k_f} = \frac{1}{k_r} + \frac{K_r}{k_2} = \frac{1}{k_r} + \frac{\exp(\alpha\varphi)}{k_{s2}}$ $\lambda = (k_f/D_r^{1/2})c_O^*$
$O + R \rightleftharpoons 2Y \quad (R_r)$ $Y + e \rightleftharpoons R \quad (R_2)$ R_r rate-determining	$k_f[c_Oc_R - c_R^2 \exp(\varphi)]$	$\frac{1}{k_f} = \frac{1}{k_r}$ $\lambda = (k_f/D_R^{1/2})c_O^*$
<i>idem</i> R_2 rate-determining	$k_f[c_O^{1/2}c_R^{1/2} - c_R \exp(\frac{1}{2}\varphi)]$	$\frac{1}{k_f} = \frac{K_r^{1/2}}{k_2} = \frac{\exp(\frac{1}{2}\alpha_2\varphi)}{k_{s2}}$ $\lambda = \frac{1}{2}(k_f/D_O^{1/2}) \exp(-\frac{1}{2}\varphi)$

^a k_f = overall forward rate constant, k_i = individual forward rate constant, K_i = individual equilibrium constant; R_1, R_2 : faradaic reactions, R_d : disproportionation reaction, R_r : recombination reaction. For faradaic reactions Butler-Volmer behavior, $k_i = k_{si} \exp(-\alpha_i \varphi_i)$, is supposed.

Table 10

Expressions for the Operational Faradaic Admittance in the Case of a Two-step Reaction with Solution-soluble Intermediate.

a. General:

$$Y_F(s) = \frac{nF}{RT} \frac{(n_1/n)\tilde{F}_1(1 - \lambda_R s^{-1/2}) + (n_2/n)\tilde{F}_2(1 + \lambda_O s^{-1/2}) + (\tilde{F}_1 \lambda_{Y_2} - \tilde{F}_2 \lambda_{Y_1})s^{-1/2}}{1 + (\lambda_O - \lambda_{Y_1} + \lambda_{Y_2} - \lambda_R)s^{-1/2} + (\lambda_O \lambda_{Y_2} + \lambda_R \lambda_{Y_1} - \lambda_O \lambda_R)s^{-1}}$$

Meaning of symbols:

$$\begin{aligned} -\tilde{F}_1 &= nF(\partial v_1/\partial \varphi)_{c_O, c_Y} & \lambda_O &= D_O^{-1/2}(\partial v_1/\partial c_O)_{E, c_Y} & \lambda_{Y_1} &= D_Y^{-1/2}(\partial v_1/\partial c_Y)_{E, c_O} \\ -\tilde{F}_2 &= nF(\partial v_2/\partial \varphi)_{c_Y, c_R} & \lambda_R &= D_R^{-1/2}(\partial v_2/\partial c_R)_{E, c_Y} & \lambda_{Y_2} &= D_Y^{-1/2}(\partial v_2/\partial c_Y)_{E, c_R} \end{aligned}$$

b. High-frequency limit: $Y_F(s) = (F/RT)[n_1\tilde{F}_1 + n_2\tilde{F}_2] = R_\infty^{-1}$

c. Low-frequency limit: $Y_F(s) = \frac{F}{RT} \frac{\tilde{F}_1(n\lambda_{Y_2} - n_1\lambda_R) + \tilde{F}_2(n_2\lambda_O - n\lambda_{Y_1})}{\lambda_O\lambda_{Y_2} + \lambda_R\lambda_{Y_1} - \lambda_O\lambda_R} s^{1/2}$

d. Limit for negligible control by diffusion of O and R:

$$\begin{aligned} Y_F(s) &= \frac{F}{RT} [n_1\tilde{F}_1 + n_2\tilde{F}_2] + \frac{F}{RT} \frac{(\tilde{F}_1 - \tilde{F}_2)(n_1\lambda_{Y_1} + n_2\lambda_{Y_2})s^{-1/2}}{1 + (\lambda_{Y_2} - \lambda_{Y_1})s^{-1/2}} \\ &= R_\infty^{-1} + R_0^{-1} \frac{1}{s^{1/2}(\lambda_{Y_2} - \lambda_{Y_1})^{-1} + 1} \end{aligned}$$

in complex notation ($s = i\omega$):

$$Y_F(i\omega) = \frac{1}{R_\infty} + \frac{1}{R_0} \frac{1}{1 + p_Y(1 + i)} = \frac{1}{R_\infty} + \frac{1}{R_0} \frac{2 + p_Y - ip_Y}{2 + 2p_Y + p_Y^2}$$

with $p_Y = (2\omega)^{1/2}/(\lambda_{Y_2} - \lambda_{Y_1})$

$$R_\infty = (RT/F)(n_1\tilde{F}_1 + n_2\tilde{F}_2)^{-1}$$

$$R_0 = (RT/F)(\lambda_{Y_2} - \lambda_{Y_1})(\tilde{F}_1 - \tilde{F}_2)^{-1}(n_1\lambda_{Y_1} + n_2\lambda_{Y_2})^{-1}$$

The complex admittance or impedance, to be found after inserting $s = i\omega$, is rather intricate and not easily translated into an equivalent circuit. Only the high-frequency and the low-frequency limiting case reduce it to (pseudo-) Randles behavior, i.e., a pure charge transfer and Warburg impedance respectively. Another limiting case, viz. negligible influence of diffusion of O and R ($\lambda_O = \lambda_R = 0$), only λ_{Y_1} and λ_{Y_2} remain) can be expressed in terms of an equivalent circuit as shown in Figure 36a, together with examples of corresponding complex plane diagrams.⁽⁹⁸⁾ Note that here the low-frequency limit is a pure resistance, with either a positive or a negative value.

The same mechanistic scheme has been treated by Hung and Smith,⁽⁹⁹⁾ taking into account the potential dependence of the parameters. Their expressions are extremely intricate, but can be shown to be identical to those

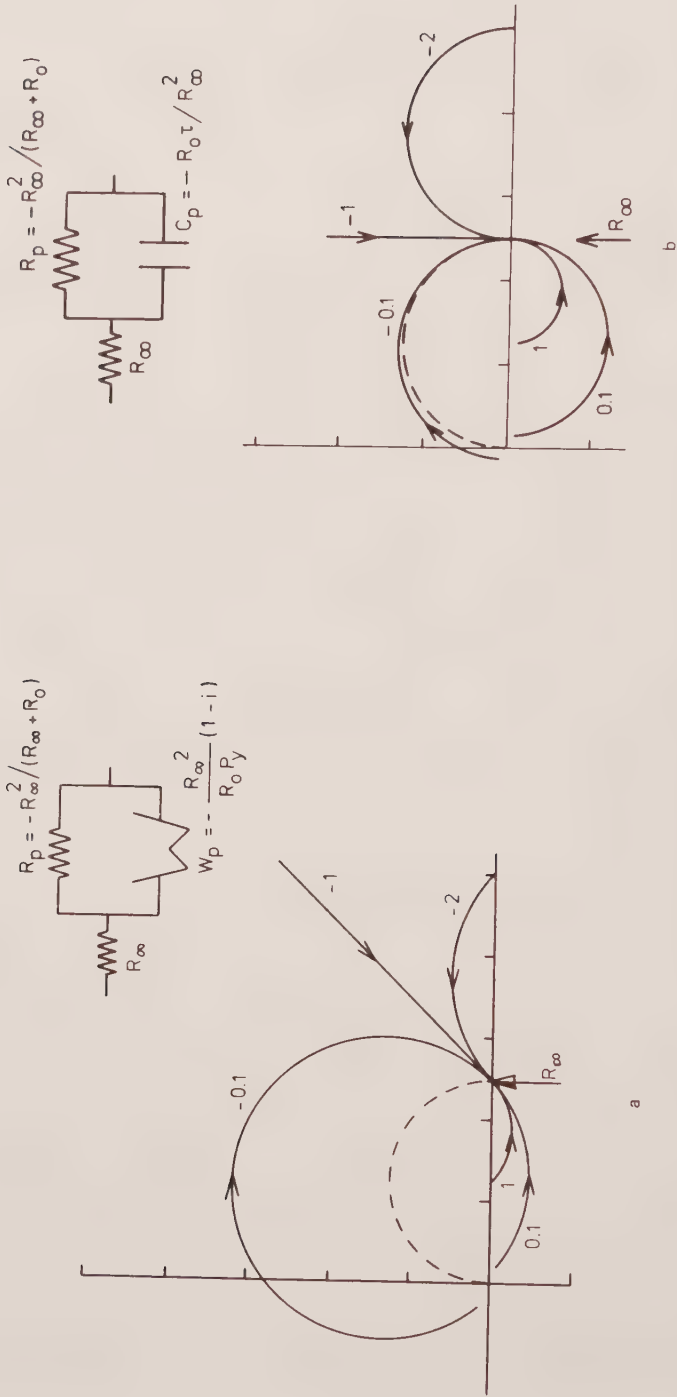


Figure 36. (a) Equivalent circuit and corresponding complex impedance plots for the limiting case d) in Table 10 (frequency variation), for different values of R_0/R_∞ , viz. 1, 0.1, -0.1, -1, -2, as indicated. The infinite frequency point is at $Z = (R_\infty, 0)$, indicated by the arrow. The dashed semi-circle represents the high-frequency behavior of R_∞ in parallel with the double layer capacity.⁽⁹⁸⁾ (b) The same for the limiting case d) in Table 11.

in Table 10 after introduction of the proper expressions for the surface concentrations.

5.3.3. Adsorbed Intermediate

In an earlier treatment,⁽¹⁰⁰⁾ it was assumed that the intermediate, instead of diffusing in the solution, is adsorbed at the interface. This is expressed in the same way as in Eqs. (117) to (119), only replacing c_Y by Γ_Y (the surface concentration) and Eq. (119c) by

$$\overline{\Delta\Gamma_Y}(s) = s^{-1}[\overline{\Delta v_1}(s) - \overline{\Delta v_2}(s)] \quad (120)$$

(in view of the relation $d\Gamma_Y/dt = \Delta v_1 - \Delta v_2$). The derivation then leads to the operational admittance shown in formulae in Table 11. Again the faradaic

Table 11

Expressions for the Operational Faradaic Admittance in the Case of a Two-step Reaction with Adsorbed Intermediate

a. General:

$$Y_F(s) = \frac{nF}{RT} \frac{(n_1/n)\tilde{F}_1(1 - \lambda_R s^{1/2}) + (n_2/n)\tilde{F}_2(1 + \lambda_O s^{-1/2}) + (\tilde{F}_1 y_2 - \tilde{F}_2 y_1)s^{-1}}{1 + (\lambda_O - \lambda_R)s^{-1/2} + (y_2 - y_1 - \lambda_O \lambda_R)s^{-1} + (\lambda_O y_2 + \lambda_R y_1)s^{-3/2}}$$

Meaning of symbols:

$\tilde{F}_1, \tilde{F}_2, \lambda_O$ and λ_R as in Table 10.

$$y_1 = (\partial v_1 / \partial \Gamma_Y)_{E, c_O} \quad y_2 = (\partial v_2 / \partial \Gamma_Y)_{E, c_R}$$

b. High-frequency limit: $Y_F(s) = (F/RT)(n_1\tilde{F}_1 + n_2\tilde{F}_2) = R_\infty^{-1}$

c. Low-frequency limit: $Y_F(s) = \frac{nF}{RT} \frac{\tilde{F}_1 y_2 - \tilde{F}_2 y_1}{\lambda_O y_2 + \lambda_R y_1} s^{1/2}$

d. Limit for negligible control by diffusion of O and R:

$$Y_F(s) = \frac{F}{RT} [n_1\tilde{F}_1 + n_2\tilde{F}_2] + \frac{F}{RT} \frac{(\tilde{F}_1 - \tilde{F}_2)(n_1 y_1 + n_2 y_2)s^{-1}}{1 + (y_2 - y_1)s^{-1}}$$

$$= R_\infty^{-1} + R_0^{-1} \frac{1}{s(y_2 - y_1)^{-1} + 1}$$

in complex notation ($s = i\omega$):

$$Y_F(i\omega) = \frac{1}{R_\infty} + \frac{1}{R_0} \frac{1}{1 + i\omega\tau} = \frac{1}{R_\infty} + \frac{1}{R_0} \frac{1 - i\omega\tau}{1 + \omega^2\tau^2}$$

with $\tau = (y_2 - y_1)^{-1}$

$$R_\infty = (RT/F)(n_1\tilde{F}_1 + n_2\tilde{F}_2)^{-1}$$

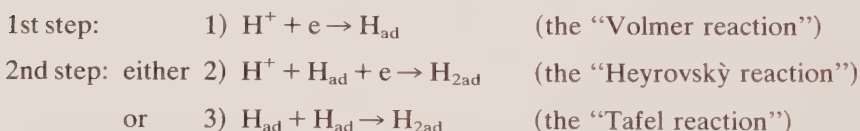
$$R_0 = (RT/F)(y_2 - y_1)(\tilde{F}_1 - \tilde{F}_2)^{-1}(n_1 y_1 + n_2 y_2)^{-1}$$

impedance reduces to a pure resistance at high frequencies and to a Warburg impedance at low frequencies. Neglect of diffusion of O and R leads to the equivalent circuit in Figure 36b, with the corresponding characteristic complex plane behavior shown in Figures 36b and 37.

Armstrong's treatment, which generalizes some earlier derivations,^(101,102) is nonrigorous in two aspects. First, adsorption at an interface may occur to a limited extent; i.e., when maximum coverage is about to be reached, it is only logical to assume that part of the intermediate is non-adsorbed and may diffuse away. Second, adsorption changes the double layer structure and has its influence on the double layer charging. It is not correct to assume that the faradaic admittance is shunted simply by the double layer capacity of the supporting electrolyte (see below).

5.3.4. Examples

A derivation for a mechanism with adsorbed intermediate was presented for the first time by Gerischer and Mehl⁽¹⁰¹⁾ *in concreto* for the possible mechanism of the hydrogen evolution reaction at various metal electrodes. The mechanism considered implies three possible reactions:



The possibility that the alternatives for the second step proceed concurrently is admitted. Further it is assumed that the circumstances are such that mass transport of H^+ is not rate-determining and also that desorption of H_2 and further removal of the gas from the electrode is fast as compared to the actual heterogeneous reactions. The set of equations to be solved is therefore:

$$\begin{aligned}
 -\Delta j_V &= F\Delta v_1 = -\tilde{F}_1\varepsilon + y_1F\Delta\Gamma_Y \\
 -\Delta j_H &= F\Delta v_2 = -\tilde{F}_2\varepsilon + y_2F\Delta\Gamma_Y \\
 -\Delta j_T &= 2F\Delta v_3 = -\tilde{F}_3\varepsilon + y_3F\Delta\Gamma_Y \\
 -\overline{\Delta j_V(s)} + \overline{\Delta j_H(s)} + \overline{\Delta j_T(s)} &= sF\overline{\Delta\Gamma_Y(s)} \\
 \Delta j_V + \Delta j_H &= \Delta j
 \end{aligned} \tag{121}$$

with identical or similar meanings of the symbols as in Table 11. The solution in the Laplace domain is

$$\frac{\overline{\Delta j(s)}}{\varepsilon(s)} = \tilde{F}_1 + \tilde{F}_2 + \frac{(\tilde{F}_1 - \tilde{F}_2 - \tilde{F}_3)(y_1 + y_2)}{s - y_1 + y_2 + y_3} \tag{122}$$

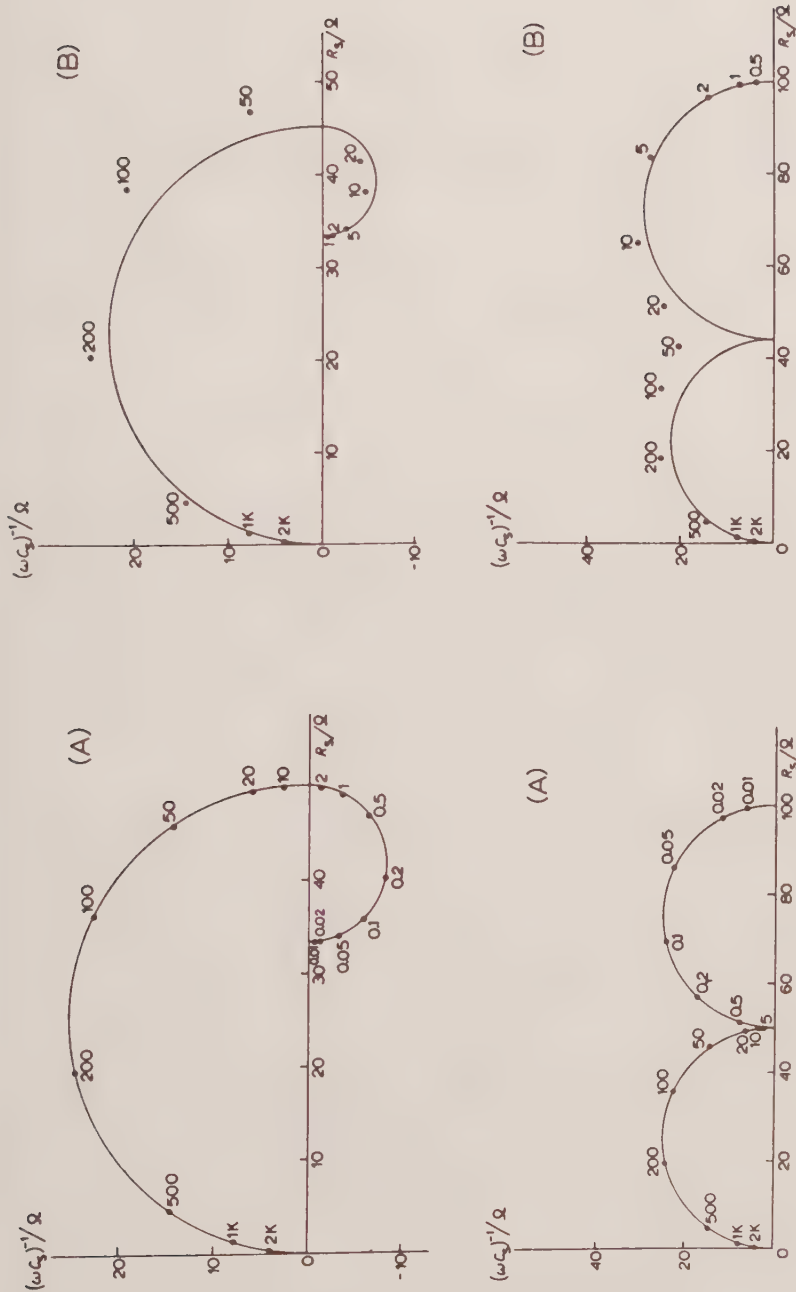


Figure 37. Complex plane plots corresponding to the case d) of Table 11 with account for the double layer capacity (frequency variation). Upper curves: $R_0 = 2R_{\infty}$; lower curves: $R_0 = -2R_{\infty}$; A: $C_d = 1000/R_{\infty}$; B: $C_d = 50/R_{\infty}$. C_d is the double layer capacity (not shown in the equivalent circuit in Fig. 36b).

which, after introduction of $s = i\omega$ and separation of the real and imaginary terms, leads to the faradaic admittance.⁽¹⁰¹⁾

$$\frac{RT}{F} Y_F = (\tilde{F}_1 + \tilde{F}_2) - \frac{a \cdot b}{b^2 + \omega^2 c_H^2} + i \frac{a \cdot \omega c_H}{b^2 + \omega^2 c_H^2} \quad (123)$$

The "adsorption capacity" $c_H = F\Gamma_m$ (Γ_m is maximum coverage) has been introduced because of the model expressions adopted for the relations between partial rates and the fractional surface coverage $\theta = \Gamma_Y/\Gamma_m^{(101)}$; in our notation

$$v_1 = k_{f1}(1 - \theta)c_{H^+} \quad (124a)$$

$$v_2 = k_{f2}\theta c_{H^+} \quad (124b)$$

$$2v_3 = k_3\theta^2 \quad \text{with } k_3 \neq f(E) \quad (124c)$$

whence

$$a = F^2 c_H'^2 [\alpha_2 k_{f2} \theta' - \alpha_1 k_{f1} (1 - \theta')] [k_{f2} - k_{f1}] \quad (125a)$$

$$b = F c_H' [k_{f1} + k_{f2}] + F_2 k_3 \theta' \quad (125b)$$

Experimental verification, in particular of the frequency dependency of the real component, was attempted at mercury, copper, and silver electrodes. In the first case no frequency dispersion was found; at the other metals the observed frequency dispersion appeared to be confused by spurious effects.

Another example is found in the early results of Epelboin and Keddam⁽¹⁰²⁾ concerning the anodic dissolution of iron in aqueous sulfuric acid. The reaction mechanism



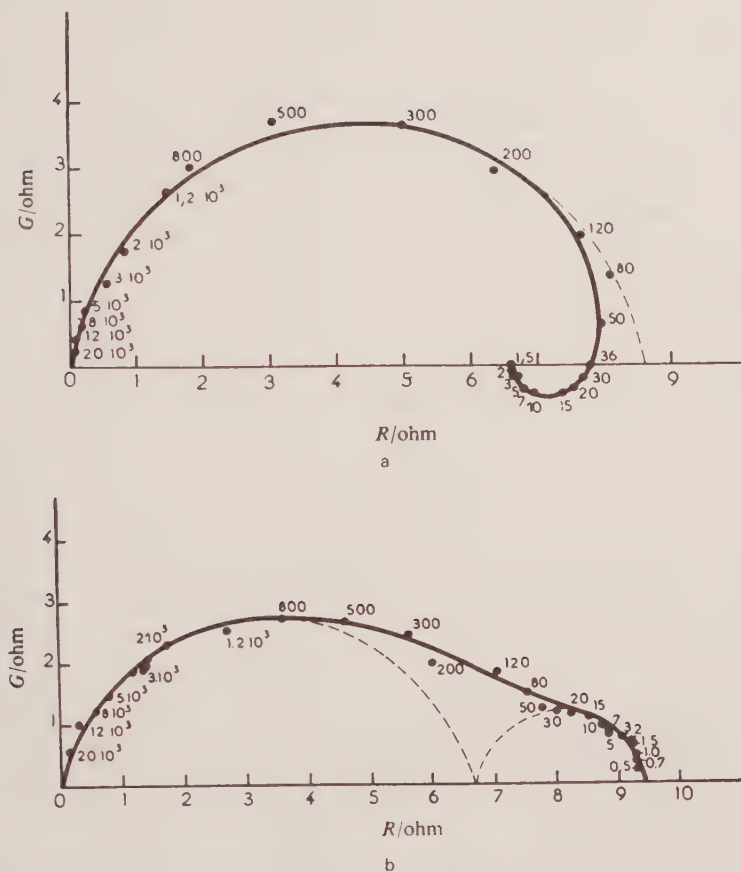
is exactly as described in Section 5.3.3. A representative complex plane plot is reproduced in Figure 38. In later studies more complex behavior was reported.

Experimental impedance studies of a solution-soluble intermediate case appear to have been limited to the trivial case where the standard potentials are well separated such as the reaction $\text{Cu(II)} \rightarrow \text{Cu(I)} \rightarrow \text{Cu(0)}$.

In the last decade some examples have been published of the more puzzling mechanism with unstable intermediates, but perhaps the first convincing evidence deduced from a.c. measurements was given in 1959 by Randles⁽¹⁰³⁾ for the reaction $\text{Cd(II)}/\text{Cd(Hg)}$. Although his data were rather inaccurate, it is very clear that the apparent transfer coefficient depends on potential, which means that k_f must be of a composite nature, as indicated in Table 9.

5.3.5. The Theory of Partial Charge Transfer

In connection with the foregoing, attention must be paid to another theory for multi-step electrode processes with adsorbed intermediates, developed by



on the applied interfacial potential, but also on the concomitant changes in the adsorbed amounts. This is expressed as follows

$$\frac{dq}{dt} = \left(\frac{\partial q}{\partial E} \right)_{\Gamma_i} \frac{dE}{dt} + \sum \left(\frac{\partial q}{\partial \Gamma_i} \right)_E \frac{d\Gamma_i}{dt} \quad (126)$$

If we again confine the illustration to a two-step mechanism



the derivative $d\Gamma_Y/dt$ is equal to $v_1 - v_2$. Therefore the *total* current $j = j_F + j_C$ is given by

$$-j = l_1 nFv_1 + l_2 nFv_2 - C_{HF} \frac{dE}{dt} \quad (127)$$

with

$$l_1 = \lambda_1 - \frac{1}{nF} \left(\frac{\partial q}{\partial \Gamma_Y} \right)_E \quad (128a)$$

$$l_2 = \lambda_2 + \frac{1}{nF} \left(\frac{\partial q}{\partial \Gamma_Y} \right)_E = 1 - l_1 \quad (128b)$$

$$C_{HF} = \left(\frac{\partial q}{\partial E} \right)_{\Gamma_Y} \quad (129)$$

The capacity C_{HF} is known as “the electrode capacity at frozen-in reaction”⁽¹⁰⁴⁾ or the “high frequency capacity”.⁽¹⁰⁷⁾

Finally, because of the unconventional nature of the elementary steps, a parameter f_i is introduced, relating the equilibrium constant K_i of each step to the potential difference $E - E^\circ$:

$$f_i = \frac{\partial \ln K_i}{\partial \varphi} \quad \text{with } \sum f_i = 1 \quad (130)$$

Just by definition

$$-\tilde{F}_i = nF \frac{\partial v_i}{\partial \varphi} = f_i nF \frac{\partial v_i}{\partial \ln K_i} \quad (131)$$

If Eqs. (127) and (129) are combined with Eqs. (119a, 119b) and Eq. (120), the problem is *mathematically* formulated as in Section 5.3.3, only some parameters having an essentially different meaning. The resulting complex interfacial admittance is derived to be

$$Y_{el} = i\omega C_{HF} + \frac{nF}{RT} \times \frac{l_1 \tilde{F}_1 + l_2 \tilde{F}_2 + (l_2 \tilde{F}_2 \lambda_O - l_1 \tilde{F}_1 \lambda_R)(i\omega)^{-1/2} + (\tilde{F}_1 y_2 - \tilde{F}_2 y_1)(i\omega)^{-1}}{1 + (\lambda_O - \lambda_R)(i\omega)^{-1/2} + (y_2 - y_1 - \lambda_O \lambda_R)(i\omega)^{-1} + (y_2 \lambda_O + y_1 \lambda_R)(i\omega)^{-3/2}} \quad (132)$$

Evidently Armstrong's equation (cf. Table 10) can be considered as a special case of Eq. (132) with $l_i = n_i/n$ and $C_{HF} = C_d$.

The parameters f_i do not appear explicitly in Eq. (132) but Lorenz has formulated an alternative expression, making use of relations resembling those of Reinmuth [see Section 4.2], for each separate step. These relations are

$$\left(\frac{\partial v_1}{\partial c_O}\right)_{\varphi, \Gamma_Y} = -\frac{1}{c'_O} \frac{\partial v_1}{\partial \ln K_1} \quad \text{or} \quad f_1 n F \lambda_O = \tilde{F}_1 / (c'_O D_O^{-1/2}) \quad (133a)$$

$$\left(\frac{\partial v_1}{\partial \Gamma_Y}\right)_{\varphi, c_O} = \frac{1-g}{\Gamma_Y} \frac{\partial v_1}{\partial \ln K_1} \quad \text{or} \quad f_1 n F y_1 = -\tilde{F}_1 (1-g) / \Gamma_Y \quad (133b)$$

$$\left(\frac{\partial v_2}{\partial c_R}\right)_{\varphi, \Gamma_Y} = \frac{1}{c'_R} \frac{\partial v_2}{\partial \ln K_2} \quad \text{or} \quad f_2 n F \lambda_R = -\tilde{F}_2 / (c'_R D_R^{-1/2}) \quad (133c)$$

$$\left(\frac{\partial v_2}{\partial \Gamma_Y}\right)_{\varphi, c_R} = -\frac{1-g}{\Gamma_Y} \frac{\partial v_2}{\partial \ln K_2} \quad \text{or} \quad f_2 n F y_2 = \tilde{F}_2 (1-g) / \Gamma_Y \quad (133d)$$

where the new parameter g is called the "isotherm factor" (for example, $g = 0$ for a Henry isotherm, but $g = \beta_Y c_Y$ for a Langmuir isotherm).

Generalization of the foregoing to an arbitrary number of steps and further consequences of the theory have been treated in several publications [see Reference (104)].

It may be noted that because of the partial charge transfer concept, the theory is also applicable to reactions involving only one electron, and even to just (nonfaradaic) specific adsorption of a charged species like iodide at a mercury electrode [Lorenz, 1967].⁽¹⁰⁸⁾ A detailed discussion on this subject has been given by Parsons.⁽¹⁰⁹⁾

5.4. Adsorption of the Reactants

As early as 1942 Brdička reported on the anomalies in the d.c. polarograms of methylene blue and showed that these could be attributed to the fact that the electro-active species were also surface active, that is they are significantly adsorbed at the interface.⁽¹¹⁰⁾ The shape of the polarograms were mathematically described by a nonrigorous solution of Fick's law, with the new boundary conditions

$$j_F = -nFD_O \left(\frac{\partial c_O}{\partial x}\right)_{x=0} + nF \frac{d\Gamma_O}{dt} = nFD_R \left(\frac{\partial c_R}{\partial x}\right)_{x=0} - nF \frac{d\Gamma_R}{dt} \quad (134)$$

This equation expresses that any flux of O or R towards or from the interface serves to maintain two processes: the faradaic charge transfer and the ad- or desorption of the species.

The first attempt to account for reactant adsorption in impedance theory was made by Laitinen and Randles,⁽¹¹¹⁾ by assuming two pathways for charge

transfer, viz. via the adsorbed species and via the non-adsorbed (diffusing) species, but neglecting the coupling between these processes imposed by Eq. (134). Derivations based on Eq. (134) were presented almost simultaneously by Llopis *et al.*^(32,112) and Senda and Delahay,⁽¹¹³⁾ and resulted in a more complex equivalent circuit, with which observed deviations from Randles behavior could be explained, see Figure 39. However, Sluyters-Rehbach and Sluyters⁽¹¹⁴⁾ pointed out the argument that apparent deviation from Randles behavior could as well be caused by the erroneous assumption that the parallel double layer capacity in the Randles circuit retained the value of that in the supporting electrolyte, even though, with the redox-couple, notoriously adsorbing species were added. In fact it could be shown that impedance measurements on the $Tl^+/Tl(Hg)$ electrode obeyed the Randles circuit, only with an increased parallel capacity. The meaning of this increase, however, remained unclear.⁽¹¹⁵⁾

The basis for the real correct treatment was finally given by Delahay,⁽¹¹⁶⁾ by stating that in addition to the coupling of the *faradaic* charge transfer process and the *nonfaradaic* adsorption process in Eq. (134), also the dependence of the nonfaradaic charging current on the latter process should be considered. In other words, the charge density on the electrode is no longer a function of only the potential but also of the surface excesses Γ_O and Γ_R ; or, via isotherms, q can be represented as a function of E , c_O , and c_R , just like the faradaic current density.

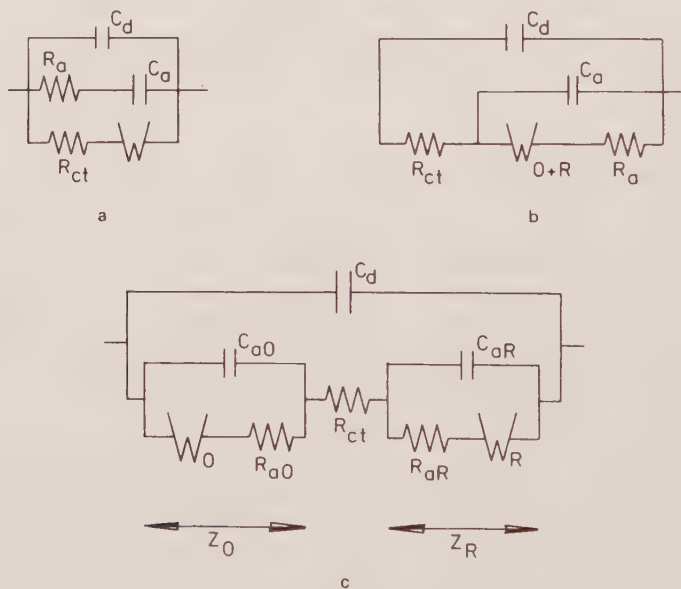


Figure 39. Equivalent circuits for some models including reactant adsorption: a) cf. Laitinen and Randles;⁽¹¹¹⁾ b) cf. Llopis *et al.*⁽¹¹²⁾; c) cf. Senda and Delahay.⁽¹¹³⁾

The consequences of this for the mathematical formulation of the equivalent circuit are rather severe. In the following we will treat the most important aspects in order to enable the reader to obtain some idea of the effects.

5.4.1. The General Admittance Expression

From the several treatments known in the literature,⁽¹¹⁶⁻¹¹⁹⁾ we follow that of Birke,⁽¹¹⁸⁾ since it is most similar to the procedures we followed in the foregoing sections. The set of equations to be solved is as follows:

$$\Delta j_F = (\partial j_F / \partial E) \Delta E + (\partial j_F / \partial c_O) \Delta c_O + (\partial j_F / \partial c_R) \Delta c_R \quad (135a)$$

$$\Delta q = (\partial q / \partial E) \Delta E + (\partial q / \partial c_O) \Delta c_O + (\partial q / \partial c_R) \Delta c_R \quad (135b)$$

$$\Delta \Gamma_O = (\partial \Gamma_O / \partial E) \Delta E + (\partial \Gamma_O / \partial c_O) \Delta c_O + (\partial \Gamma_O / \partial c_R) \Delta c_R \quad (135c)$$

$$\Delta \Gamma_R = (\partial \Gamma_R / \partial E) \Delta E + (\partial \Gamma_R / \partial c_O) \Delta c_O + (\partial \Gamma_R / \partial c_R) \Delta c_R \quad (135d)$$

and, already transformed into the Laplace domain:

$$\mathcal{L} \Delta j_F = s^{1/2} n F D_O^{1/2} \mathcal{L} \Delta c_O + s n F \mathcal{L} \Delta \Gamma_O \quad (136)$$

$$-s \mathcal{L} (\Delta \Gamma_O + \Delta \Gamma_R) = s^{1/2} \mathcal{L} (D_O^{1/2} \Delta c_O + D_R^{1/2} \Delta c_R) \quad (137)$$

$$\mathcal{L} \Delta j = \mathcal{L} \Delta j_F + \mathcal{L} \Delta j_c = \mathcal{L} \Delta j_F + s \mathcal{L} \Delta q \quad (138)$$

This set-up implies the following assumptions:

- charge transfer proceeds as $O + ne \rightleftharpoons R$ without stable intermediates
- semi-infinite linear diffusion is the only mode of mass transfer
- E , c_O , and c_R , are the only independent variables (the partial derivatives in Eq. (135) are to be read as $(\partial j_F / \partial E)_{c_O, c_R}$, etc.).

The solution of Eq. (135) through (138) is only a matter of patient elimination of all Δc 's and $\Delta \Gamma$'s and Δq to obtain the relation between $\mathcal{L} \Delta j$ and $\mathcal{L} \Delta E$. The result is shown in Table 12 in terms of twelve parameters. The complexity of the result discourages the separation of the real and imaginary terms. However, the admittance expression has been formulated quite generally and simplification is feasible. For example, the actual number of parameters is reduced to nine if the adsorbed species are assumed to be in equilibrium. This does not help very much, but if in addition it is supposed that cross-derivatives of the double layer parameters are negligible, i.e.,

$$\delta_R = \varepsilon_O = \kappa_O = \kappa_R = \ddot{E}_{\Gamma_O} = \ddot{E}_{\Gamma_R} = 0$$

Table 12

Expressions for the Operational Admittance in the Case of Reversible Reactant Adsorption Accompanying the Reaction $O + ne \rightleftharpoons R$

a. Finite rate of charge transfer:

$$[Y_{el}(s) - \tilde{E}_q s] \times \{(\delta_O \varepsilon_R - \delta_R \varepsilon_O)s + (\delta_O + \varepsilon_R)s^{1/2} + (\lambda_O \gamma_R - \lambda_R \gamma_O + 1) + (\lambda_O - \lambda_R)s^{-1/2}\} \\ = R_{cl}^{-1} \times \{(\delta_O \varepsilon_R - \delta_R \varepsilon_O - \kappa_O \gamma_R - \kappa_R \gamma_O)s + (\delta_O - \varepsilon_R + \kappa_O - \kappa_R)s^{1/2} + 1\} + \\ \tilde{E}_{\Gamma_O} s \{(\kappa_R \varepsilon_O - \kappa_O \varepsilon_R)s - \kappa_O s^{1/2} + (\lambda_O \varepsilon_R - \lambda_R \varepsilon_O) + \lambda_O s^{-1/2}\} + \\ \tilde{E}_{\Gamma_R} s \{(\kappa_O \delta_R - \kappa_R \delta_O)s - \kappa_R s^{1/2} + (\lambda_R \delta_O + \lambda_O \delta_R) + \lambda_R s^{-1/2}\}$$

Meaning of symbols: $\gamma_O = \delta_O + \varepsilon_O$; $\gamma_R = \delta_R + \varepsilon_R$

$$\tilde{E}_q = \left(\frac{\partial q}{\partial E} \right)_{c_O, c_R}, \quad \tilde{E}_{\Gamma_O} = nF \left(\frac{\partial \Gamma_O}{\partial E} \right)_{c_O, c_R}, \quad \tilde{E}_{\Gamma_R} = nF \left(\frac{\partial \Gamma_R}{\partial E} \right)_{c_O, c_R}, \quad R_{cl}^{-1} = \left(\frac{\partial j_F}{\partial E} \right)_{c_O, c_R}, \\ \kappa_O = \frac{D_O^{-1/2}}{nF} \left(\frac{\partial q}{\partial c_O} \right)_{E, c_R}, \quad \delta_O = D_O^{-1/2} \left(\frac{\partial \Gamma_O}{\partial c_O} \right)_{E, c_R}, \quad \varepsilon_O = D_O^{-1/2} \left(\frac{\partial \Gamma_R}{\partial c_O} \right)_{E, c_R}, \quad \lambda_O = -\frac{D_O^{-1/2}}{nF} \left(\frac{\partial j_F}{\partial c_O} \right)_{E, c_R}, \\ \kappa_R = \frac{D_R^{-1/2}}{nF} \left(\frac{\partial q}{\partial c_R} \right)_{E, c_O}, \quad \delta_R = D_R^{-1/2} \left(\frac{\partial \Gamma_O}{\partial c_R} \right)_{E, c_O}, \quad \varepsilon_R = D_R^{-1/2} \left(\frac{\partial \Gamma_R}{\partial c_R} \right)_{E, c_O}, \quad \lambda_R = -\frac{D_R^{-1/2}}{nF} \left(\frac{\partial j_F}{\partial c_R} \right)_{E, c_O}$$

b. Additional thermodynamic relations from adsorption equilibrium:

$$c'_R D_R^{1/2} \delta_R = c'_O D_O^{1/2} \varepsilon_O$$

$$c'_O D_O^{1/2} \kappa_O = (RT/nF) \tilde{E}_{\Gamma_O}$$

$$c'_R D_R^{1/2} \kappa_R = (RT/nF) \tilde{E}_{\Gamma_R}$$

c. Infinite rate of charge transfer (a.c. reversible limit):

$$Y_{el}(s) = \frac{s^{1/2}}{\sigma 2^{1/2}} - \tilde{E}_{\Gamma} s \frac{\chi_\psi s^{1/2} + nF(\sigma_R/\sigma)}{\gamma_\psi s^{1/2} + 1} + \tilde{E}_q^* s$$

Meaning of symbols: $\sigma = \sigma_O + \sigma_R$; $\psi = c_O D_O^{1/2} + c_R D_R^{1/2}$

$$\tilde{E}_q^* = \left[\frac{\partial(q + nF\Gamma_O)}{\partial E} \right]_\psi, \quad \tilde{E}_{\Gamma} = \left[\frac{\partial(\Gamma_O + \Gamma_R)}{\partial E} \right]_\psi, \quad \sigma_R = \frac{RT}{n^2 F^2 2^{1/2}} \frac{1}{c'_R D_R^{1/2}}, \\ \chi_\psi = \left[\frac{\partial(q + nF\Gamma_O)}{\partial \psi} \right]_E, \quad \gamma_\psi = \left[\frac{\partial(\Gamma_O + \Gamma_R)}{\partial \psi} \right]_E, \quad \sigma_O = \frac{RT}{n^2 F^2 2^{1/2}} \frac{1}{c'_O D_O^{1/2}}$$

a surveyable equation for $Y_{el}(s)$ can be derived:

$$Y_{el}(s) = R_{cl}^{-1} \left(1 - \frac{\lambda_R s^{-1/2}}{1 + \varepsilon_R s^{1/2}} + \frac{\lambda_O s^{-1/2}}{1 + \delta_O s^{1/2}} \right)^{-1} + sC_d \quad (139)$$

which obeys the equivalent circuit of Figure 40a.

5.4.2. The A.C. Reversible Limit

Another simplification is possible if charge transfer is so fast that it becomes non-rate-determining. In principle this could be achieved by careful adaptation of the general expression, but it is more elegant to start the derivation anew,

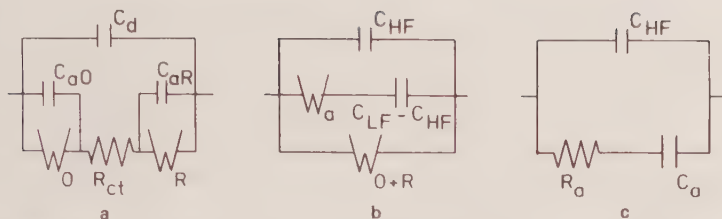


Figure 40. Equivalent circuits accounting for reactant adsorption in some limiting cases: a) cf. Eq. (139); b) cf. Eq. (144); c) cf. Eq. (150).

with recognition of the following points:

- the Nernst equation holds for both d.c. and a.c. surface concentrations and replaces Eq. (135a).
- as a consequence only two of the variables c_O , c_R , and E are independent and the Taylor expansions will contain two terms, e.g., in Δc_O and Δc_R , or ΔE and Δc_O , or ΔE and a combination of Δc_O and Δc_R .

Although the choice appears to be arbitrary, it has been shown [Timmer, 1968]⁽¹²⁰⁾ that it is convenient to choose as independent variables E and $\psi = c_O D_O^{1/2} + c_R D_R^{1/2}$. The set of equations to be solved then becomes:

$$\frac{\Delta c_O}{c_O} \frac{D_O^{1/2} c'_O + D_R^{1/2} c'_R}{D_R^{1/2} c'_R} - \frac{\Delta \psi}{D_R^{1/2} c'_R} - \frac{nF}{RT} \Delta E = 0 \quad (140a)$$

$$\Delta q = (\partial q / \partial E)_\psi \Delta E + (\partial q / \partial \psi)_E \Delta \psi \quad (140b)$$

$$\Delta \Gamma_O = (\partial \Gamma_O / \partial E)_\psi \Delta E + (\partial \Gamma_O / \partial \psi)_E \Delta \psi \quad (140c)$$

$$\Delta \Gamma_R = (\partial \Gamma_R / \partial E)_\psi \Delta E + (\partial \Gamma_R / \partial \psi)_E \Delta \psi \quad (140d)$$

together with Eqs. (136) to (138). The result is also given in Table 12 in terms of six parameters. However, two of these can be eliminated by thermodynamic relations for adsorption equilibrium. This is done most favorably by considering an alternative Taylor expansion for the composite variable $q^* = q + nF\Gamma_O$; viz.

$$\Delta q^* = (\partial q^* / \partial E)_\Gamma \Delta E + (\partial q^* / \partial \Gamma)_E \Delta \Gamma \quad (141)$$

where $\Gamma = \Gamma_O + \Gamma_R$. Then with Eqs. (140c) and (140d) we have

$$\Delta q^* = [(\partial q^* / \partial E)_\Gamma + (\partial q^* / \partial \Gamma)_E (\partial \Gamma / \partial E)_\psi] \Delta E + (\partial q^* / \partial \Gamma)_E (\partial \Gamma / \partial \psi)_E \Delta \psi \quad (142)$$

so that evidently [cf. Eqs. (140b) and (140c)]:

$$(\partial q^* / \partial \psi)_E = \chi_\psi = \gamma_\psi (\partial q^* / \partial \Gamma)_E$$

and

$$(\partial q^* / \partial E)_\psi = \tilde{E}_{q^*} = (\partial q^* / \partial E)_\Gamma + (\tilde{E}_\Gamma \chi_\psi / \gamma_\psi) \quad (143)$$

If this is substituted into the expression in Table 12(c), the total electrode admittance becomes

$$Y_{el}(s) = \frac{s^{1/2}}{\sigma 2^{1/2}} + s(C_{LF} - C_{HF}) \frac{1}{\gamma_\psi s^{1/2} + 1} + sC_{HF} \quad (144)$$

with

$$C_{LF} = \tilde{E}_{q^*} - nF(\sigma_R/\sigma)\tilde{E}_\Gamma \quad (144a)$$

$$C_{HF} = (\partial q^*/\partial E)_\Gamma \quad (144b)$$

With $s = i\omega$ and $u = \gamma_\psi(2\omega)^{1/2}$ the complex electrode admittance $Y = Y' + iY''$ is given by⁽¹²⁰⁾

$$Y'_{el} = \frac{\omega^{1/2}}{2\sigma} + \omega(C_{LF} - C_{HF}) \frac{u}{u^2 + 2u + 2} \quad (145a)$$

$$Y''_{el} = \frac{\omega^{1/2}}{2\sigma} + \omega(C_{LF} - C_{HF}) \frac{u + 2}{u^2 + 2u + 2} + \omega C_{HF} \quad (145b)$$

Equations (144) and (145) obey the equivalent circuit of Figure 40b.

Equation (145) describes the interfacial admittance in terms of four parameters. Among these, σ is determined in the usual way by the reactant concentrations and the d.c. potential [cf. Eq. (44)]; u can be expressed also in terms of the reactant concentrations and the potential as soon as a certain adsorption isotherm for O and R is adopted as a model. However, this is not the case with C_{LF} and C_{HF} , because these parameters contain the partial derivatives of an inseparable combination of the surface excesses Γ_O and Γ_R and the charge density q , with respect to potential. In other words, a model is needed for an explicit expression of the potential dependence of q in the presence of the adsorbed reactants.

Such a model can be obtained using thermodynamic relations derived from the electrocapillary equation for the ideally reversible electrode,⁽¹²¹⁾ following arguments formulated by Wijnhorst *et al.*⁽¹²²⁾ The essential expression derived by these authors reads

$$\begin{aligned} q^* = q^0 + \left[\frac{RT}{nF} \frac{d \ln \beta_O}{dE} + 1 \right] \int_0^{c'_O} nF \left(\frac{\partial \Gamma^*}{\partial c'_O} \right)_{\beta_O \beta_R c'_R} dc'_O \\ + \frac{RT}{nF} \frac{d \ln \beta_R}{dE} \int_0^{c'_R} nF \left(\frac{\partial \Gamma^*}{\partial c'_R} \right)_{\beta_O \beta_R c'_O} dc'_R \end{aligned} \quad (146)$$

where q^0 is the charge density in the absence of the adsorbing species, β_O and β_R are the adsorption coefficients, and c'_O and c'_R the mean surface concentrations. So, $q^* = q + nF\Gamma_O$ is determined by the nature of the adsorption isotherms (via $\partial \Gamma^*/\partial c_O$ and $\partial \Gamma^*/\partial c_R$) and the potential dependence of the adsorption coefficients therein.

5.4.3. The Limiting Case of Strong Adsorption of Both O and R

A final simplification will be treated here, based on the following assumptions^(1,2,3):

- the faradaic charge transfer takes place practically exclusively between the O and R species in the adsorbed state
- both O and R are so strongly adsorbed that the minor changes in Γ_O and Γ_R caused by a perturbation do not involve a significant change in the corresponding surface concentrations c_O and c_R ; in other words the a.c. fluxes of O and R are zero (or negligible).

Physically the latter condition means that the adsorption obeys any adsorption isotherm with an infinite adsorption coefficient. Nevertheless, it can be argued that under equilibrium conditions Γ_O and Γ_R obey a "Nernstian" relationship of the form

$$\ln \Gamma_O / \Gamma_R = (nF/RT)(E - E^\circ) - \ln (\beta_O / \beta_R)$$

where β_O and β_R denote the adsorption coefficients.

The set of equations to be solved is reduced to

$$\Delta j_F = (\partial j_F / \partial E)_{\Gamma_O, \Gamma_R} \Delta E + (\partial j_F / \partial \Gamma_O)_{E, \Gamma_R} \Delta \Gamma_O + (\partial j_F / \partial \Gamma_R)_{E, \Gamma_O} \Delta \Gamma_R \quad (147a)$$

$$\Delta q = (\partial q / \partial E)_{\Gamma_O, \Gamma_R} \Delta E + (\partial q / \partial \Gamma_O)_{E, \Gamma_R} \Delta \Gamma_O + (\partial q / \partial \Gamma_R)_{E, \Gamma_O} \Delta \Gamma_R \quad (147b)$$

$$\mathcal{L} \Delta j_F = snF \mathcal{L} \Delta \Gamma_O = -snF \mathcal{L} \Delta \Gamma_R \quad (148)$$

$$\mathcal{L} \Delta j_C = s \mathcal{L} \Delta q \quad (149)$$

Combination of Eq. (147a) and Eq. (148) leads to the relation

$$\mathcal{L} \Delta j_F / \mathcal{L} \Delta E = \overline{\Delta j_F}(s) / \overline{\Delta E}(s) = [R_a + (sC_a)^{-1}]^{-1} \quad (150a)$$

and similarly Eq. (147b) with Eqs. (148) and (149) gives

$$\overline{\Delta j_C}(s) / \overline{\Delta E}(s) = q_\Gamma [R_a + (sC_a)^{-1}]^{-1} + sC_{HF} \quad (150b)$$

with

$$R_a = 1 / (\partial j_F / \partial E)_{\Gamma_O, \Gamma_R} \quad (151a)$$

$$C_a = [(\partial j_F / \partial \Gamma_R)_{E, \Gamma_O} - (\partial j_F / \partial \Gamma_O)_{E, \Gamma_R}] R_a \quad (151b)$$

$$q_\Gamma = [(\partial q / \partial \Gamma_O)_{E, \Gamma_R} - (\partial q / \partial \Gamma_R)_{E, \Gamma_O}] / nF \quad (151c)$$

$$C_{HF} = (\partial q / \partial E)_{\Gamma_O, \Gamma_R} \quad (151d)$$

q_Γ might be supposed to be negligibly small, but of course this is not necessarily so. The equivalent circuit of Eq. (150) is given in Figure 40c and appears to be a limiting form of the Senda-Delahay circuit, i.e., with the Warburg impedances infinitely large.

5.4.4. Deviation from Randles Behavior

In order to compare the admittance expressions derived with those for Randles behavior they will be inspected graphically by means of plots of $Y_{el}/\omega^{1/2}$ and $(Y_{el}'' - \omega C_d)/\omega^{1/2}$ versus $\omega^{1/2}$. This is done in Figure 41.

The effects of reactant adsorption are most strongly emphasized by comparing Randles behavior and behavior of the a.c. reversible limit [Eqs. (145)]. Instead of a decrease with increasing frequency due to the presence of charge transfer control, the plotted functions exhibit an increase due to the occurrence of reactant adsorption. From this it might be inferred that charge transfer and reactant adsorption counteract each other. This is confirmed by the plots made from the simplified equation (139): at low frequency the increasing tendency and at high frequency the decreasing tendency is followed.

In view of these conclusions it is useful to consider possible limiting behavior of three cases at low and high frequencies, and to inspect whether "pseudo-Randles behavior" could be observed under certain conditions. This is summarized in Table 13.

Also, the potential dependence of the admittance may be quite different from Randles behavior. As an example, this is shown for the a.c. reversible case in Figure 42.⁽¹²⁴⁾ The calculations are based on the assumption that the adsorption obeys a Langmuir isotherm, which leads to the potential dependence of C_{LF} and $u/\omega^{1/2}$ in Figure 43.

5.5. Nonfaradaic Heterogeneous Processes

All cases discussed in Sections 5.3 and 5.4 concern processes where charge is exchanged between the electrode and the species involved. It is possible to extrapolate some of these to processes *not involving charge transfer*, just by assigning the appropriate meaning to the parameters. Two examples will be treated briefly in this section.

5.5.1. Adsorption of a Single Non-electro-active Species

The process considered is the adsorption-desorption of a species A, with a finite rate v and in addition controlled by diffusion. For this case the formulae of Section 5.3.5 can be used, reduced in the following way:

- only one step needs to be considered, so, parameters with index $i > 1$ equal zero
- no (partial) charge transfer occurs, so $l_1 nF = -(\partial q / \partial \Gamma)_E$

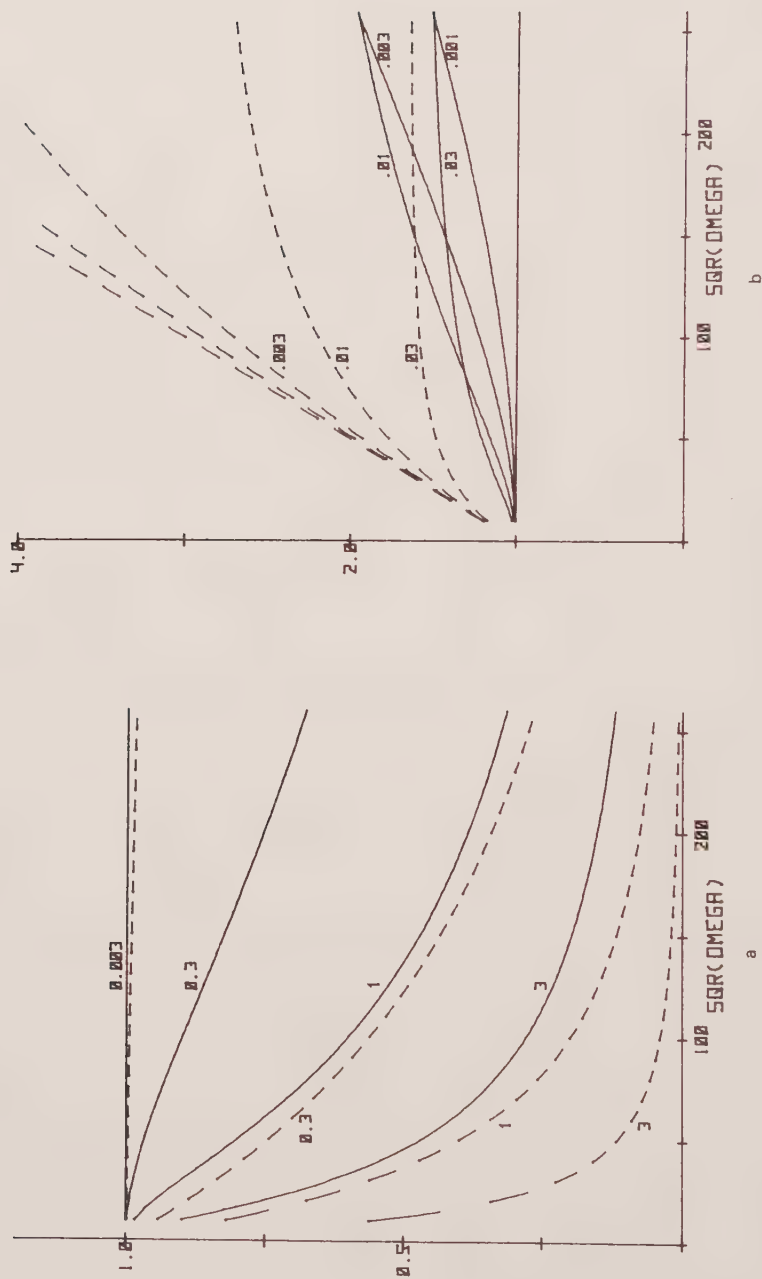
Thus simplification of Eq. (132) gives

$$Y_{el}(i\omega) = i\omega C_{HF} + \left(\frac{\partial q}{\partial \Gamma_A} \right)_E \left(\frac{\partial v}{\partial E} \right)_{c_A, \Gamma} \frac{1}{1 + \lambda_A(i\omega)^{-1/2} - y_A(i\omega)^{-1}} \quad (152)$$

where $\lambda_A = D_A^{-1/2}(\partial v / \partial c_A)_{E, \Gamma_A}$ and $y_A = (\partial v / \partial \Gamma_A)_{E, c_A}$. The high-frequency

Table 13
Limiting Forms of the Complex Interfacial Admittance Expressions for Reactant Adsorption, Exhibiting Pseudo-Randles Behavior

Model	High-frequency limit $Y_{el}(i\omega) \rightarrow$	Low-frequency limit $Y_{el}(i\omega) \rightarrow$
general Table 12a	$R_{ct}^{-1} \left[1 + \frac{\kappa_O \varepsilon_R - \kappa_R \varepsilon_O + \kappa_O \delta_R - \kappa_R \delta_O}{\delta_O \varepsilon_R - \delta_R \delta_O} \right] + i\omega \left[\frac{\tilde{E}_q - \tilde{E}_{\Gamma_O}}{\delta_O \varepsilon_R - \delta_R \varepsilon_O} - \frac{\kappa_R \delta_O - \kappa_O \delta_R}{\varepsilon_R \delta_O - \varepsilon_O \delta_R} \right]$ $= R_{ct}^{-1} [1 + q_\Gamma] + i\omega C_{HF}$	$\frac{R_{ct}^{-1}}{\lambda_O - \lambda_R} \frac{\omega^{1/2}}{2^{1/2}} (1+i) + i\omega \times \left[\frac{\tilde{E}_q + \tilde{E}_{\Gamma_O}}{\lambda_O - \lambda_R} \frac{\lambda_O}{\lambda_O - \lambda_R} - \frac{E_{\Gamma_R}}{\lambda_O - \lambda_R} \frac{\lambda_R}{\lambda_O - \lambda_R} \right]$ $= (2\sigma)^{-1} \omega^{1/2} (1+i) + i\omega C_{LF}$ $R_{ct}^{-1} \left[1 + \frac{(\lambda_O - \lambda_R) 2^{1/2}}{\omega^{1/2} (1+i)} \right]^{-1} + i\omega C_d$ $= \frac{\omega^{1/2}}{2\sigma} \frac{p+1+i}{p^2+2p+p} + i\omega C_d$ with $p = R_{ct}/\sigma\omega^{-1/2}$ $i\omega(C_a + C_{HF}) = i\omega C_{LF}$ $(2\sigma)^{-1} \omega^{1/2} (1+i) + i\omega C_{LF}$
Eq. (139)	$R_{ct}^{-1} + i\omega C_d$	
Eq. (150) a.c. reversible	$R_a^{-1} (1 + q_\Gamma) + i\omega C_{HF}$ $[(2\sigma)^{-1} + (C_{LF} - C_{HF}) (2^{1/2} \gamma_\psi)^{-1}] \omega^{1/2} (1+i) + i\omega C_{HF}$	
Eq. (144)		



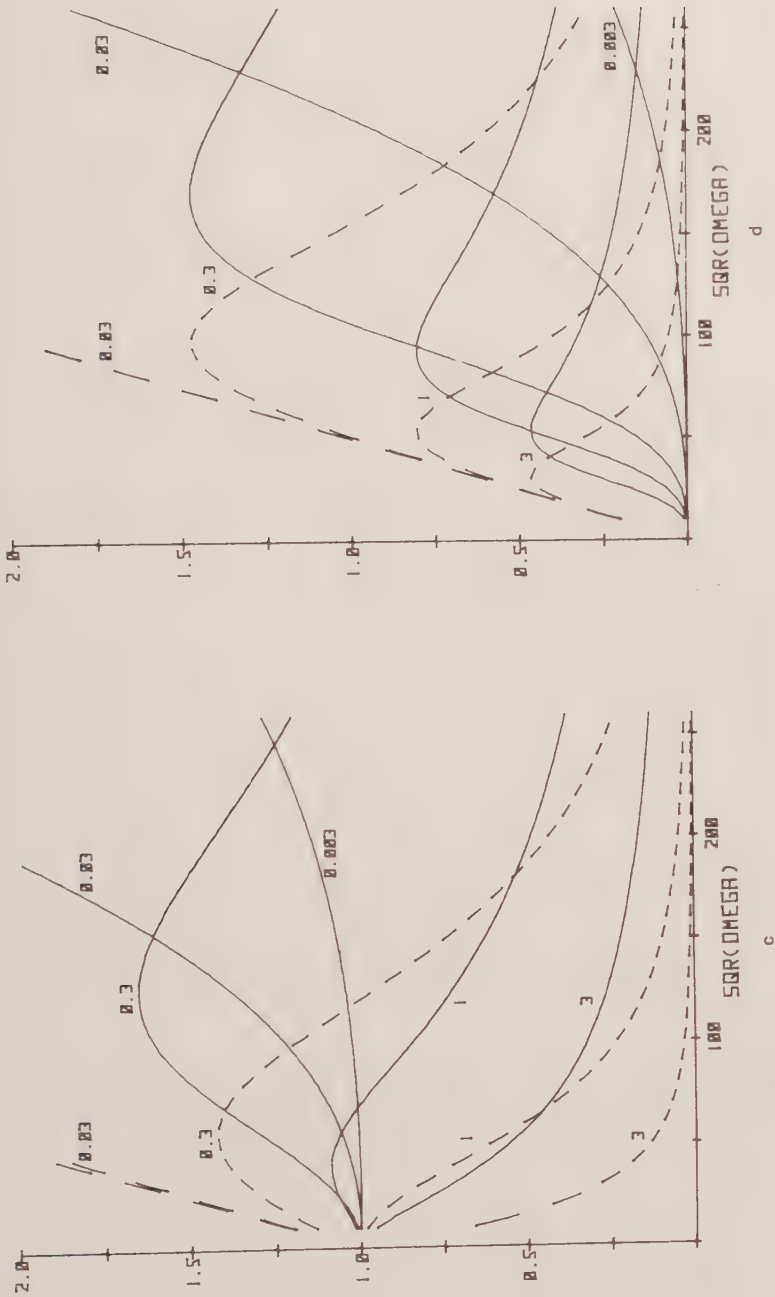


Figure 41. Typical behavior of $Y'/\omega^{1/2}$ (solid curves) and $(Y'' - \omega C_d)/\omega^{1/2}$ (dashed curves) in different cases. (a) Randles behavior: $\sigma = 50$, $R_{ct} = 0.003$, 0.3, 1, 3; (b) a.c. reversible with reactant adsorption: $\sigma = 50$, $C_{LF} - C_{HF} = 200$, $C_{HF} - C_d = 0$, $u' = 0.001$, 0.0003, 0.01, 0.03; (c) nonreversible with reactant adsorption, cf Figure 40a, $\sigma_O = \sigma_R = 50$, $c_{aO} = c_{aR} = 100$, $R_{ct} = 0.003$, 0.03, 0.3, 1, 3 (d) very strong adsorption of both reactants: $C_a = 200 \mu F cm^{-2}$, $R_a = 0.003$, 0.03, 0.3, 1, 3.

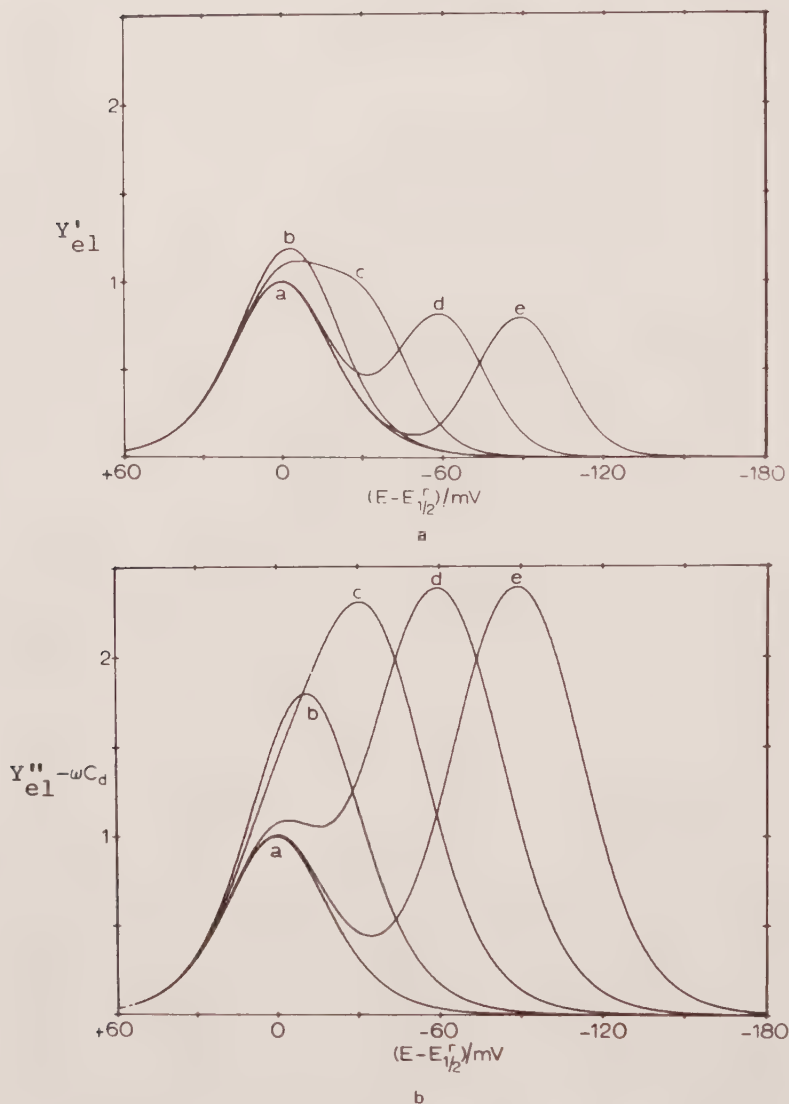


Figure 42. Potential dependence of (a) the in-phase component Y' and (b) the quadrature component Y'' of the interfacial admittance. A.c. reversible electrode reaction with Langmuirian adsorption of Ox. The varied parameter is $\beta_O c_O^*$: (a) 0, (b) 1, (c) 10, (d) 100, (e) 1000. The polarograms are normalized by dividing by the peak height of (a).

limit of Y_{el} is $i\omega C_{HF}$. The low-frequency limit is also purely capacitive, viz. $i\omega C_{LF}$, given by

$$C_{LF} = C_{HF} - \left(\frac{\partial q}{\partial \Gamma_A} \right)_E \left(\frac{\partial v}{\partial E} \right)_{c_A, \Gamma_A} \left(\frac{\partial \Gamma_A}{\partial v} \right)_{E, c_A} \quad (153)$$

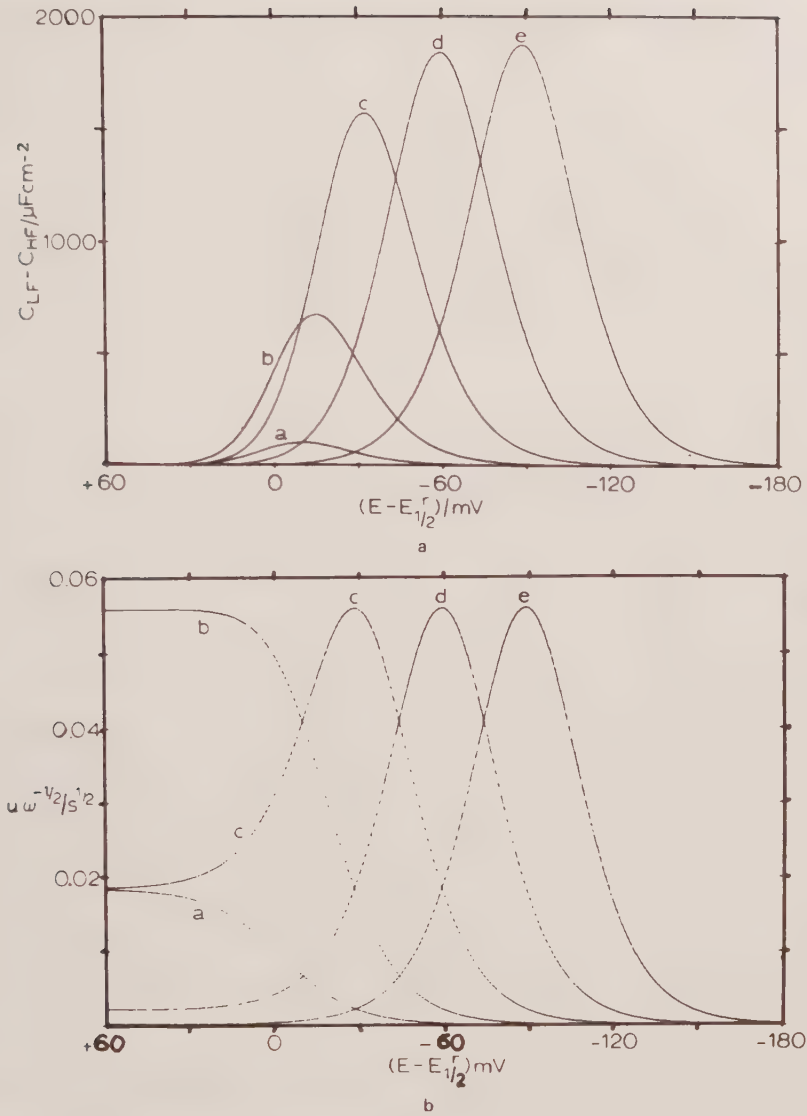


Figure 43. (a) The adsorption parameter $C_{LF} - C_{HF}$ as a function of potential. $\Gamma_m = 0.5 \times 10^{-9} \text{ mole cm}^{-2}$; $D_O = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$; $\beta_O c_O^*$: (a) 0.1, (b) 1, (c) 10, (d) 100, (e) 1000. (b) The adsorption parameter $u / \omega^{1/2}$ as a function of potential for the same data.

which, with application of the rule of implicit functions, can be shown to be

$$C_{LF} = C_{HF} + \left(\frac{\partial q}{\partial \Gamma_A} \right)_E \left(\frac{\partial \Gamma_A}{\partial E} \right)_{c_A, v} \tag{154}$$

The equivalent circuit of Eq. (152) is a parallel connection of the capacity C_{HF} and an impedance Z_a , which with some manipulation can be written as⁽¹²⁵⁾

$$Z_a = R_a + \frac{\gamma_c \omega^{-1/2} (1-i)}{C_{LF} - C_{HF}} - \frac{i}{\omega (C_{LF} - C_{HF})} \quad (155)$$

with

$$R_a = -(\partial \Gamma_A / \partial v) / (C_{LF} - C_{HF}) \quad (155a)$$

$$\gamma_c = (2/D_A)^{1/2} (\partial \Gamma_A / \partial c)_{E,v} \quad (155b)$$

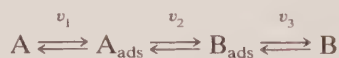
If the adsorption-desorption process were infinitely fast ($R_a = 0$), the expression for Z_a could also have been derived as a limiting case of the formulae in Section 5.4, with $\sigma = \sigma_R = \infty$.⁽³³⁾

5.5.2. Nonfaradaic Electrode Reactions

The existence of a phase boundary between a metal electrode and an electrolyte solution may give rise to the occurrence of *chemical* reactions, i.e., without transfer of charge across the interface, as well.

First, it is feasible that an overall faradaic process involves one or more chemical steps, either preceding or following electron transfer, or intermediate between two charge transfer steps. This is easily accounted for applying the principles of Section 5.3 to the proper number of steps, faradaic *plus* nonfaradaic, and setting the charge transferred in the nonfaradaic step equal to zero. In fact one example is the Tafel-reaction treated in Section 5.3.4. Another example is the final step in an electrocrystallization reaction, e.g., represented as $M^+ + e \rightleftharpoons M_{ad} \rightleftharpoons M$. The admittance for this case follows from Table 11 by setting $n_2 = 0$, $n_1 = n$, and $\lambda_R = 0$. In addition it may be supposed that the rate of crystallization does not depend on potential, i.e., $\tilde{F}_2 = 0$. This leads to a fairly simple equivalent circuit, consisting of the charge transfer resistance in series with the Warburg impedance for diffusion of M^+ , and an impedance $Z_R = (R_p^{-1} + j\omega C_p)^{-1}$ replacing the Warburg impedance for the *Red* component.⁽¹²⁶⁾ This is the most simple model for electrocrystallization; other more sophisticated treatments include for example adatom transport (surface diffusion).^(127,128)

Another possibility is the occurrence of a heterogeneous reaction $A \rightleftharpoons B$ via adsorbed A and B, which may be considered as a model for heterogeneous catalysis.⁽¹²⁹⁾ The mechanism is described as

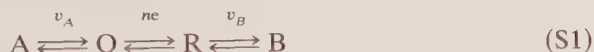


with only v_1 and v_3 dependent on potential, and mass transport of A and B controlled by diffusion. If, for the sake of simplicity, it is assumed that v_2 is large (A_{ads} and B_{ads} virtually in equilibrium), the problem is in fact reduced to the case described by Eq. (132), but with $l_1 nF \equiv \partial q / \partial (\Gamma_A + \Gamma_B)$ and $\tilde{F}_1 = RT(\partial v_i / \partial E)$. An alternative approach is to assume that v_1 and v_3 are large (the adsorption processes both in equilibrium) and then the theory is

identical to that in section 5.4, leading to similar admittance expressions in the various cases treated there.

5.6. Coupled Homogeneous Reactions

Thus far the only mode of supply and removal of reacting species has been supposed to be diffusional mass transport. Sometimes additional supply or removal can occur via chemical reactions, taking place between electro-active species (O, R) and electro-inactive species (A, B) present in the phases at either side of the interface. A simple example is represented by the typical scheme:



Again the impedance concept is most suitable to demonstrate the implications of the reactions $A \rightleftharpoons O$ and $R \rightleftharpoons B$ accompanying the diffusion process. In the Laplace domain the relations between the interfacial concentration fluctuations and the faradaic a.c. current are

$$\mathcal{L}\Delta C_O = \frac{\mathcal{L}\Delta j_F}{nFD_O^{1/2}} \left[\frac{K_A}{K_A + 1} s^{-1/2} + \frac{1}{K_A + 1} (s + k_A)^{-1/2} \right] \quad (156a)$$

$$\mathcal{L}\Delta C_R = -\frac{\mathcal{L}\Delta j_F}{nFD_R^{1/2}} \left[\frac{K_B}{K_B + 1} s^{-1/2} + \frac{1}{K_B + 1} (s + k_B)^{-1/2} \right] \quad (156b)$$

where D_O , D_R are the *mean* diffusion coefficients, K_A , K_B the equilibrium constants, and k_A , k_B equal the sum of the forward and backward rate constants [see Appendix II]. These expressions specify implicitly the operator $\tilde{y}_1$ in Eq. (106) and are to replace Eq. (112) in the Randles formulae. Of course this is applicable in all the more or less complex cases treated in Sections 5.3 to 5.5, but we will confine ourselves to a case of single charge transfer without reactant adsorption, and consequently invoke, as before, the first-order Taylor expansion for j_F :

$$\mathcal{L}\Delta j_F = R_{ct}^{-1} \mathcal{L}\Delta E - (nFD_O^{1/2}) \lambda_O \mathcal{L}\Delta C_O - (nFD_R^{1/2}) \lambda_R \mathcal{L}\Delta C_R$$

With $s = i\omega$, and $\sigma_O = R_{ct} \lambda_O / 2^{1/2}$, $\sigma_R = -R_{ct} \lambda_R / 2^{1/2}$, we obtain for the complex faradaic impedance $Z_F = \mathcal{L}\Delta j_F / \mathcal{L}\Delta E$ describing mechanism (S1):

$$\begin{aligned} Z_F = R_{ct} + & \left[\sigma_O \frac{K_A}{K_A + 1} + \sigma_R \frac{K_B}{K_B + 1} \right] \omega^{-1/2} (1 - i) \\ & + \frac{\sigma_O \omega^{-1/2}}{K_A + 1} \frac{[(g^2 + 1)^{1/2} + g]^{1/2} - i[(g^2 + 1)^{1/2} - g]^{1/2}}{(g^2 + 1)^{1/2}} \\ & + \frac{\sigma_R \omega^{-1/2}}{K_B + 1} \frac{[(h^2 + 1)^{1/2} + h]^{1/2} - i[(h^2 + 1)^{1/2} - h]^{1/2}}{(h^2 + 1)^{1/2}} \end{aligned} \quad (157)$$

with $g = k_A / \omega$ and $h = k_B / \omega$.

Both the frequency dependence and the d.c. potential dependence will be discussed briefly.

5.6.1. Frequency Dependence

Due to the accompanying reactions, part of the Warburg impedances of O and R have been replaced by the complex impedances expressed in the third and fourth term in Eq. (157). In view of the earliest derivation of such an impedance by Gerischer,⁽¹³⁰⁾ it seems a good idea to name it the "Gerischer impedance", Z_G . The frequency dependence of Z_G is visualized in Figure 44, and is characterized by the maximum in Z''_G at $\omega = 3^{1/2}k_i$ and the high- and low-frequency limits:

- (a) if $k_A/\omega \ll 1$, then $Z_{G,O}$ reduces to $[\sigma_O\omega^{-1/2}/(K_A + 1)](1 - i)$ and converges with the Warburg term to $\sigma_O\omega^{-1/2}(1 - i)$; if in addition $k_B/\omega \ll 1$, *pseudo-Randles behavior* is attained, i.e., $Z_F = R_{ct} + (\sigma_O + \sigma_R)\omega^{-1/2}(1 - i)$.
- (b) if $k_A/\omega \gg 1$, then the imaginary component of $Z_{G,O}$ vanishes and the real component becomes frequency independent; if in addition $k_B/\omega \gg 1$, *pseudo-Randles behavior* will be found, according to

$$Z_F = R_{ct} + \frac{\sigma_O k_A^{-1/2}}{K_A + 1} + \frac{\sigma_R k_B^{-1/2}}{K_B + 1} + \left(\sigma_O \frac{K_A}{K_A + 1} + \sigma_R \frac{K_B}{K_B + 1} \right) \omega^{-1/2}(1 - i) \quad (158)$$

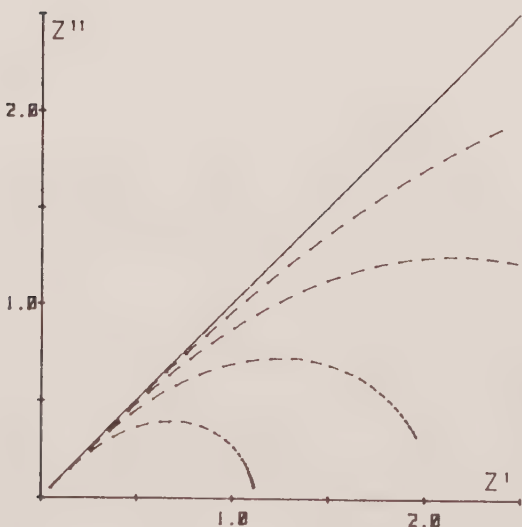


Figure 44. Complex plane diagram of the impedance Z_G . C.f. Eq. (157) for fixed σ_O , σ_R and varied $k_A = k_B$.

The resistive terms in σ_O and σ_R vanish if $k_A, k_B \rightarrow \infty$ and/or $K_A, K_B \rightarrow \infty$. This limit of Eq. (158) may be considered as real Randles behavior, since then the Warburg coefficient relates to the total concentrations $c'_O + c'_A$ and $c'_R + c'_B$ (*vide infra*).

N.B. Of course it is possible that only one of the two redox components, e.g., O, is involved in a chemical reaction. In that case k_B (or h) should be taken as zero, which restores the original Warburg impedance $\sigma_R \omega^{-1/2}(1-i)$. The complex plane diagram of the total impedance for this case is shown in Figure 45.

Another interesting case is that of the catalytic mechanism, $O + ne \rightleftharpoons R$ accompanied by $R + C \rightleftharpoons O$, for which the impedance is given by

$$Z_F = R_{ct} + (\sigma_O + \sigma_R) \omega^{-1/2} \frac{[(c^2 + 1)^{1/2} + c]^{1/2} - i[(c^2 + 1)^{1/2} - c]^{1/2}}{(c^2 + 1)^{1/2}} \quad (159)$$

with $c = k_c/\omega$ (see Appendix II). The shape of the complex plane plot will be as in Figure 44.

5.6.2. Potential Dependence

A similar formalism as in Section 2.5 will be developed, but only with the expanding plane model (for the dropping mercury electrode). Some attention must be paid to the definition of the standard potential and the corresponding reversible half-wave potential. At equilibrium the concentrations of the

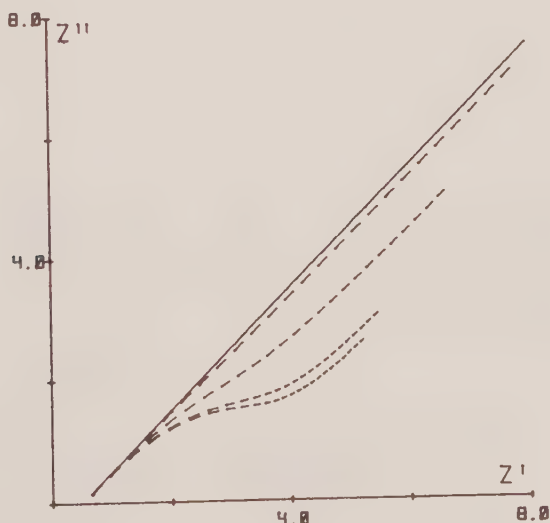


Figure 45. Complex plane diagram of the faradaic impedance in the case that one reactant is involved in a chemical reaction. Cf. Eq. (157) with $k_B = 0$ and varied value of k_A .

four species will be related by

$$\begin{aligned}c_O/c_A &= c_O^*/c_A^* = K_A \\c_R/c_B &= c_R^*/c_B^* = K_B \\E_{eq} &= E^\circ + (RT/nF) \ln c_O^*/c_R^* \\&= E_T^\circ + (RT/nF) \ln [(c_O^* + c_A^*)/(c_R^* + c_B^*)]\end{aligned}$$

whence

$$E_T^\circ = E^\circ + (RT/nF) \ln [K_A/(K_A + 1)] - (RT/nF) \ln [K_B/(K_B + 1)]$$

Practically it is convenient to refer the potential E to E_T° , via the quantities Φ and Z defined analogously to φ and ζ . The relationships between these quantities are given in Table 14. The "d.c. reversible" situation is now defined as that situation where both charge transfer and the chemical reactions are fast as compared to diffusion, so that the d.c. surface concentrations virtually obey the relations

$$(c'_O + c'_A)/(c'_R + c'_B) = \exp \Phi, \quad c'_O/c'_A = K_A, \quad c'_R/c'_B = K_B$$

The corresponding "reversible" parameters $R_{ct,\infty}$, $\sigma_{O,\infty}$, and $\sigma_{R,\infty}$ are also defined in Table 14.

Any deviation from this behavior, caused by the finite rate of both coupled reactions, is incorporated in the function $F(t)$:

$$\frac{\sigma_O}{\sigma_{O,\infty}} = \frac{\sigma_R}{\sigma_{R,\infty}} = \frac{R_{ct}}{R_{ct,\infty}} = F(t)^{-1} \quad (160)$$

Again there is a "rigorous" expression in $F(t)^{(131)}$ and an expression derived via the diffusion layer approximation.⁽¹³²⁾ The procedure to find these expressions is briefly as follows. Reverse transformation of the Laplace functions for $\bar{c}_P$ and $\bar{c}_O$ (expanding plane model) delivers $c'_P(t)$ and $c'_O(t)$ in the form of convolution integrals. The integral for c'_O can be approximated, if $kt > 10$, by

$$k^{1/2} K c_O(t) = (3\pi t/7)^{1/2} j_F(t)/(nFD^{1/2}) \quad (161)$$

Substitution of this relation, together with the integral for $c'_P(t)$, into the rate equation, $j_F = k_f[c'_O - c'_R \exp \varphi]$, leads to the Matsuda-Ayabe solution, as formulated in Table 14. Combination of Eq. (161) with the approximate solution for $c'_P(t)$:

$$c'_P(t) = (3\pi t/7)^{1/2} j_F(t)/(nFD^{1/2}) \quad (162)$$

leads to approximate expressions for c'_O , *casu quo* c'_R , and with the rate equation, to the approximate $F(t)$ function.

The mentioned expressions and some limiting forms are collected in Table 14.

Table 14

The Potential Dependence of the Faradaic Parameters in the Case of Coupled Homogeneous Reactions

a) Definitions of symbols:

$$\exp(\varphi) = \exp[(nF/RT)(E - E^\circ)], \quad \exp(\xi) = (D_R/D_O)^{1/2} \exp(\varphi)$$

$$\exp(\Phi) = \frac{K_B}{K_B + 1} \frac{K_A + 1}{K_A} \exp(\varphi), \quad \exp(Z) = (D_R/D_O)^{1/2} \exp(\Phi)$$

$$W = K_A/(K_A + 1), \quad K_A = \tilde{k}_A/\tilde{k}_A$$

$$k_A = \tilde{k}_A + \tilde{k}_A, \quad b_O = (K_A k_A^{1/2})^{-1}, \quad a_O = b_O + (3\pi t/7)^{1/2}$$

$$k_B = \tilde{k}_B + \tilde{k}_B, \quad b_R = (K_B k_B^{1/2})^{-1}, \quad a_R = b_R + (3\pi t/7)^{1/2}$$

$$\lambda_{ct} = (Wk_f/D_O^{1/2})[1 + \exp(Z)]$$

$$\lambda_f = [1 + \exp(Z)]/[b_O + b_R \exp(Z)]$$

$$\lambda^{-1} = \lambda_{ct}^{-1} + \lambda_f^{-1}, \quad \psi(\lambda t^{1/2}) = \text{Matsuda-Abaya function, see Table 3.}$$

b) Reversible expressions ($k_f, k_A, k_B \rightarrow \infty$):

$$R_{ct,\infty} = \frac{RTD_O^{1/2}}{n^2 F^2 Wk_f} \frac{1 + \exp(-Z)}{(c_O^* + c_A^*)D_O^{1/2} + (c_R^* + c_B^*)D_R^{1/2}}$$

$$\frac{Wk_f}{(2D_O)^{1/2}} R_{ct,\infty} = \sigma_O \frac{K_A}{K_A + 1} = \sigma_R \frac{K_B}{K_B + 1} \exp(-Z)$$

c) General: $R_{ct,\infty}/R_{ct} = F(t)$

$$F(t) = 1 + \frac{(c_O^* + c_A^*)D_O^{1/2} - (c_R^* + c_B^*)D_R^{1/2}}{(c_O^* + c_A^*)D_O^{1/2} + (c_R^* + c_B^*)D_R^{1/2}} \times G(t)$$

$$G(t) = \frac{[\alpha \exp(-Z) - (1 - \alpha)]D_O^{1/2}/(Wk_f) + b_R - b_O}{b_O + b_R \exp(Z) + D_O^{1/2}/(Wk_f)} \times \psi(\lambda t^{1/2})$$

("rigorous" approach)

$$G(t) = \frac{[\alpha \exp(-Z) - (1 - \alpha)]D_O^{1/2}/(Wk_f) + a_R - a_O}{a_O + a_R \exp(Z) + D_O^{1/2}/(Wk_f)}$$

(diffusion-layer approach)

The similar nature of the $F(t)$ function in the cases of only charge transfer control and of chemical kinetics control necessitates that the analysis of impedance measurements be conducted with some care, especially when pseudo-Randles behavior prevails. Detailed discussions can be found in the literature,^(133,134) as well as theoretical treatments of more intricate mechanisms.^(7,135,136,137)

5.7. Conclusion

The themes discussed in this section are a plain demonstration of the possible complexity of the interfacial admittance or impedance in its dependency on both frequency and d.c. potential. It may be doubted whether it is

always possible to decide unambiguously which case is prevailing. Anyway the remarks about data analysis and choice of input variables made in Sections 2.6 and 2.7 are the more relevant, knowing that so many realistic details in a mechanism are possible.

In this respect we feel it important to emphasize that the effects of these details on the frequency spectrum in our impedance studies must be equally present in the (transient) response of the other small-amplitude relaxation techniques. For, the Laplace domain solutions, which we frequently have used, are generally applicable to all the methods based on the linearized current-voltage equation. To find the eventual response-time relation is only a matter of algebra, though often with very involved mathematical expressions. With modern computers, this need not be a real disadvantage, but it seems to be justified to state that sine wave perturbation and response detection is preferable, unless very special circumstances (e.g., an extremely unstable object) require application of one of the pulse techniques.

Appendix I

AI.1. Complex Impedance and Admittance

When the current is given by

$$\Delta I = I_m \sin(\omega t + \varepsilon), \quad \Delta I(t < 0) = 0 \quad (\text{AI.1})$$

and the voltage response by

$$\Delta V = I_m [Z' \sin(\omega t + \varepsilon) - Z'' \cos(\omega t + \varepsilon)] \quad (\text{AI.2})$$

this means that

$$\Delta V = Z' \Delta I - (Z''/\omega) d\Delta I/dt \quad (\text{AI.3})$$

Then

$$\mathcal{L}[\Delta V] = \overline{\Delta V}(s) = [Z' - (s/\omega)Z'']\overline{\Delta I}(s) + (Z''/\omega)\Delta I_{t=0} \quad (\text{AI.4})$$

and since

$$\mathcal{L}[\Delta I] = \overline{\Delta I}(s) = I_m \frac{\omega \cos \varepsilon + s \sin \varepsilon}{\omega^2 + s^2}$$

one has for $s = i\omega$

$$\frac{\overline{\Delta V}(i\omega)}{\overline{\Delta I}(i\omega)} = Z' - iZ'' \quad (\text{AI.5})$$

In a similar way it can be shown that

$$\frac{\overline{\Delta I}(i\omega)}{\overline{\Delta V}(i\omega)} = Y' + iY'' = \frac{Z' + iZ''}{(Z')^2 + (Z'')^2} \quad (\text{AI.6})$$

AI.2. Input-Output Relation Including Transient Behavior

Application of Laplace transformation to the general relation of Eq. (1) for linear systems leads to

$$\begin{aligned} \bar{y}(s) = \bar{x}(s) & \frac{\sum_{j=0}^n a_{n-j} s^j}{\sum_{j=0}^m b_{m-j} s^j} - \frac{\sum_{k=0}^{n-1} \sum_{j=k}^{n-1} a_{n-(j+1)} \left(\frac{d^k x}{dt^k} \right)_{t=0} s^j}{\sum_{j=0}^m b_{m-j} s^j} \\ & + \frac{\sum_{k=0}^{m-1} \sum_{j=k}^{m-1} b_{m-(j+1)} \left(\frac{d^k y}{dt^k} \right) s^j}{\sum_{j=0}^m b_{m-j} s^j} \end{aligned} \quad (\text{AI.7})$$

This expression can be decomposed in partial fractions, generally written as

$$\begin{aligned} \bar{y}(s) = \bar{x}(s) & \left\{ \frac{A}{s-a} + \frac{B}{s-b} + \frac{C}{s-c} + \dots \right\} \\ & - \left\{ \frac{P}{s-a} + \frac{Q}{s-b} + \frac{R}{s-c} + \dots \right\} \end{aligned} \quad (\text{AI.8})$$

where $a, b, c, \dots$ are roots of the polynomial equation $\sum_{j=0}^m b_{m-j} s^j = 0$ ($a, b, c, \dots$ are negative).

Reverse transformation of the second term between brackets leads to a summation of

$$P \exp(at) + Q \exp(bt) + R \exp(ct) + \dots \quad (\text{AI.9})$$

Reverse transformation of the products $\bar{x}(s) \times A/(s-a)$, etc. for $x(t) = I_m \sin(\omega t + \varepsilon)$ leads to a summation of convolution integrals:

$$I_m A \int_0^t \exp[a(t-u)] \sin(\omega u + \varepsilon) du + \dots \quad (\text{AI.10})$$

The solution of this integral is most easily found by using the identities

$$\begin{aligned} \sin \xi &= \frac{1}{2i} \{ \exp(i\xi) - \exp(-i\xi) \} \\ \cos \xi &= \frac{1}{2} \{ \exp(i\xi) + \exp(-i\xi) \} \end{aligned} \quad (\text{AI.11})$$

The result for Eq. (AI.10) is

$$\begin{aligned} I_m A & \left\{ \left[\frac{-a}{\omega^2 + a^2} \sin(\omega t + \varepsilon) - \frac{\omega}{\omega^2 + a^2} \cos(\omega t + \varepsilon) \right] \right. \\ & \left. - \left[\frac{-a}{\omega^2 + a^2} \sin \varepsilon - \frac{\omega}{\omega^2 + a^2} \cos \varepsilon \right] \exp(at) \right\} \end{aligned} \quad (\text{AI.12})$$

So, the complete solution for $y(t)$ is the sum of three kinds of terms:

- (i) the "steady state" terms, which can be taken together as

$$I_m[Z' \sin(\omega t + \varepsilon) - Z'' \cos(\omega t + \varepsilon)] \quad (\text{AI.13})$$

- (ii) a summation of transient terms corresponding to each relaxation time contained in the system and depending on the starting level of the input signal ($I_{t=0} = I_m \sin \varepsilon$)
- (iii) similar transient terms depending on the time derivatives of input and output at $t = 0$. In not too complex cases, the problem may be formulated in such a way that these terms are zero.

AI.3. Transient Behavior of the Faradaic Process

For semi-infinite linear diffusion, again with $\Delta j_F = j_{F,m} \sin(\omega t + \varepsilon)$, the solution emanating from Eq. (28) is the well-known integral equation

$$\begin{aligned} & -[\alpha c'_O + (1 - \alpha)c'_R \exp \varphi] \frac{nF}{RT} \Delta E \\ & = \frac{j_{F,m}}{nFk_f} \sin(\omega t + \varepsilon) + \frac{j_{F,m}}{nF} [D_O^{-1/2} + D_R^{-1/2} \exp \varphi] \\ & \quad \times \int_0^t \frac{\sin(\omega t + \varepsilon - \omega u)}{(\pi u)^{1/2}} du \end{aligned} \quad (\text{AI.14})$$

The convolution integral is decomposed into

$$\text{C.I.} = \sin(\omega t + \varepsilon) \times \int_0^t \frac{\cos \omega u}{(\pi u)^{1/2}} du - \cos(\omega t + \varepsilon) \times \int_0^t \frac{\sin \omega u}{(\pi u)^{1/2}} du \quad (\text{AI.15})$$

The integrals in Eq. (AI.15) are known as Fresnel integrals, which can be expressed as⁽¹³⁸⁾

$$C = (2/\omega)^{1/2} \left[\frac{1}{2} + \frac{K + H}{\pi^{1/2}} \sin \omega t - \frac{K - H}{\pi^{1/2}} \cos \omega t \right]$$

and

$$S = (2/\omega)^{1/2} \left[\frac{1}{2} - \frac{K - H}{\pi^{1/2}} \sin \omega t - \frac{K + H}{\pi^{1/2}} \cos \omega t \right] \quad (\text{AI.16})$$

respectively (C refers to the cosine integral, S to the sine integral). $K + H$ and $K - H$ are functions of two arguments, in this case $(\omega t/2)^{1/2}$, $(\omega t/2)^{1/2}$.⁽¹³⁸⁾ The numerical Tables given in the quoted reference reveal that for $\omega t > 2\pi$, $K - H$ approaches zero and $(K + H)/\pi^{1/2}$ approaches $(2\omega t)^{-1/2}$ [see also Reference (139)]. Combining Eqs. (AI.15) and (AI.16) gives for the

convolution integral:

$$\begin{aligned} \text{C.I.} = (2\omega)^{-1/2} [\sin(\omega t + \varepsilon) - \cos(\omega t + \varepsilon)] \\ - (2/\omega)^{1/2} \pi^{-1/2} [(K - H) \sin \varepsilon - (K + H) \cos \varepsilon] \end{aligned} \quad (\text{A1.17})$$

The term in $K - H$ decays rapidly, but the term in $K + H$ decays slowly with increasing time.

Appendix II. Laplace Domain Solutions for Some Mass Transfer Problems

For all the problems to be treated, the procedure of substitution of variables will be followed⁽³⁾ which transfers the constituting differential equations to a "Fick's law" form:

$$D \frac{\partial^2 u}{\partial z^2} = \frac{\partial u}{\partial t} \quad (\text{AII.1})$$

where u is related to the concentration c and z to the distance x from the interface in either phase. For any problem we have the initial condition

$$u = u^* \quad \text{for } t = 0 \quad (\text{AII.2})$$

The Laplace transform of Eq. (AII.1) is

$$D \frac{\partial^2 \bar{u}}{\partial z^2} - s\bar{u} + u^* = 0 \quad (\text{AII.3})$$

where $\bar{u} = \bar{u}(z, s)$ is the Laplace transform of $u = u(z, y)$. The general solution of this linear differential equation is

$$\bar{u}(z, s) = s^{-1}u^* + M(s) \exp[-zs^{1/2}/D^{1/2}] + N(s) \exp[+zs^{1/2}/D^{1/2}] \quad (\text{AII.4})$$

The integration constants $M(s)$ and $N(s)$ have to be found by considering (a) the particular meaning of u and z , and (b) the particular boundary conditions for each problem separately. This will be done in the following paragraphs.

All.1. Semi-infinite Linear Diffusion

The original differential equation being of the form of Eq. (AII.1), we have $u = c$ and $z = x$, and the boundary conditions

$$\bar{u}(\infty, s) = s^{-1}u^*$$

$$nFD(\partial\bar{u}/\partial z)_{z=0} = \mp \bar{j}_F(s)$$

from which it follows that $N(s) = 0$ and $M(s) = \pm s^{-1/2} \bar{j}_F(s)/(nFD^{1/2})$. Consequently the surface concentration $\bar{c}(0, s) = \bar{u}(0, s)$ is

$$\bar{c}(0, s) = s^{-1}c^* \pm s^{-1/2} \bar{j}_F(s)/(nFD^{1/2}) \quad (\text{AII.5})$$

where, because of the adopted sign convention, the plus sign pertains to c_O and the minus sign to c_R .

All.2. Bounded Linear Diffusion

Also for this case $u = c$ and $z = x$, but the first boundary condition is different:

$$\bar{u}(\delta, s) = s^{-1}u^*$$

$$nFD(\partial\bar{u}/\partial z)_{z=0} = \mp \bar{j}_F(s)$$

Introduction of these conditions into Eq. (AII.4) gives the result:

$$M(s) = -N(s) \exp(2\delta s^{1/2}/D^{1/2})$$

$$N(s)[1 + \exp(2\delta s^{1/2}/D^{1/2})] = \mp s^{-1/2} \bar{j}_F(s)/(nFD^{1/2})$$

whence, with $\bar{c} = \bar{u}$:

$$\bar{c}(0, s) = s^{-1}c^* \mp \frac{1 - \exp(2\delta s^{1/2}/D^{1/2})}{1 + \exp(2\delta s^{1/2}/D^{1/2})} s^{-1/2} \bar{j}_F(s)/(nFD^{1/2}) \quad (\text{AII.6})$$

Note that with $s = i\omega$ the complex exponentials give rise to the oscillating character of the diffusional impedance, with δ and ω .

All.3. Semi-infinite Spherical Diffusion

Equation (AII.1) is in accordance with the original differential equation for spherically symmetrical diffusion if $u = cr$ and $z = r$, where r is the distance from the center of a stationary spherical electrode with a radius r_0 . The boundary conditions are, in the Laplace domain:

$$\bar{u}(\infty, s) = s^{-1}u^*$$

$$nFD[(\partial\bar{u}/\partial z)_{z=r_0} - u(r_0, s)/r_0] = \mp r_0 \bar{j}_F(s)$$

Elaboration of the second boundary condition must be performed with some attention to the algebraic definitions. Since again $N(s)$ must be zero, we obtain

$$M(s) \exp(-r_0 s^{1/2}/D^{1/2})[(s^{1/2}/D^{1/2}) + r_0^{-1}] = \pm r_0 \bar{j}_F(s)/(nFD)$$

and consequently $\bar{u}(r_0, s)/r_0 = \bar{c}(r_0, s)$ is

$$\bar{c}(r_0, s) = s^{-1} c^* \pm \frac{r_0}{1 + (r_0 s^{1/2}/D^{1/2})} \bar{j}_F(s)/(nFD) \quad (\text{AII.7})$$

which, as it should, reduces to Eq. (AII.5) if $r_0 \rightarrow \infty$.

AII.4. Dropping Mercury Electrode

Although not necessary for the impedance expressions *per se*, we also mention the way to solve the d.c. diffusion problem towards an expanding planar electrode as a model for the DME. Instead of Eq. (AII.1), in this case we seek the solution of the differential equation

$$D \frac{\partial^2 u}{\partial z^2} = \frac{\partial u}{\partial y}$$

with $z = xt^{2/3}$ and $y = (3/7)t^{7/3}$, while $u = c$. In Laplace form, the solution for $\bar{c}(0, s)$ is, of course, identical to Eq. (AII.5). The reverse transformation leads to the relation between $c(0, y)$ and j_F :

$$\int_0^y j_F(y) dy = \pm \frac{nFD^{1/2}}{\pi^{1/2}} \int_0^y \frac{c(0, t) - c^*}{(y - \tau)^{1/2}} d\tau \quad (\text{AII.8})$$

This integral equation can be solved with the aid of an additional relation, i.e., the charge transfer equation. If it is desired to avoid this, the integral on the right-hand side of Eq. (AII.8) can be approximated by taking $c(0, t) - c^*$ out under the integral sign. This leads to the well-known diffusion-layer solution.

AII.5. Coupled Homogeneous Reaction

The differential equations to be solved, e.g., for c_O , are

$$\begin{aligned} \frac{\partial c_A}{\partial t} &= D_A \frac{\partial^2 c_A}{\partial x^2} - \vec{k}_A c_A + \tilde{k}_A c_O \\ \frac{\partial c_O}{\partial t} &= D_O \frac{\partial^2 c_O}{\partial x^2} + \vec{k}_A c_A - \tilde{k}_A c_O \end{aligned} \quad (\text{AII.9})$$

where $\vec{k}_A$ and $\tilde{k}_A$ are the rate constants of the forward and backward chemical reaction, respectively. Further quantities needed are: $K_A = \vec{k}_A/\tilde{k}_A$ and $k_A = \vec{k}_A + \tilde{k}_A$.

The usual approach is to invoke auxiliary concentration functions $c_T = c_A + c_O$ and $c_S = c_A - c_O/K$, and to assume in addition $D_A = D_O$. If the latter is not realistic, a more exact result may be obtained by defining the following auxiliary functions:

$$c_P = (D_A/D_M)c_A + (D_O/D_M)c_O \quad (\text{AII.10a})$$

$$c_O = c_A - K_A^{-1}c_O \quad (\text{AII.10b})$$

with

$$D_M = (D_A + K_A D_O)/(K_A + 1) \quad (\text{AII.11})$$

It can be shown with Eq. (AII.9) that, to a quite good approximation, c_P and c_O obey the differential equations

$$\frac{\partial c_P}{\partial t} \approx D_M \frac{\partial^2 c_P}{\partial x^2} \quad (\text{AII.12a})$$

$$\frac{\partial c_O}{\partial t} \approx D_M \frac{\partial^2 c_O}{\partial x^2} - k_A \frac{D_M^2}{D_O D_A} c_O \quad (\text{AII.12b})$$

The terms omitted in these equations are respectively: $K_A(D_A - D_O)/(K_A + 1)D_M \times \partial c_O/\partial t$ and $D_M(D_O^{-1} - D_A^{-1})/(K_A + 1) \times \partial c_P/\partial t$.

The Laplace transforms of Eq. (AII.12) lead to

$$\bar{c}_P(x, s) = s^{-1}c_P^* + P(s) \exp[-xs^{1/2}/D^{1/2}] \quad (\text{AII.13a})$$

$$\bar{c}_O(x, s) = Q(s) \exp[-x(s+k)^{1/2}/D^{1/2}] \quad (\text{AII.13b})$$

(since for $x \rightarrow \infty$ $c_P = c_P^*$ and $c_O = 0$). With the boundary conditions

$$nFD_M(\partial \bar{c}_P/\partial x)_{x=0} = -\bar{j}_F(s)$$

$$nFD_M(\partial \bar{c}_O/\partial x)_{x=0} = +\bar{j}_F(s)(D_M/D_O)K_A^{-1}$$

the substitutions $P(s) = s^{1/2}\bar{j}_F(s)/(nFD_M^{1/2})$ and $(D_O/D_M)Q(s) \times K_A = -(s+k)^{1/2}\bar{j}_F(s)/(nFD_M^{1/2})$ are easily found.

From the definitions of the auxiliary functions in Eq. (AII.10) it can be derived that

$$\bar{c}_O(0, s) = \frac{K_A}{K_A + 1} [\bar{c}_P(0, s) - (D_A/D_M)\bar{c}_O(0, s)] \quad (\text{AII.14})$$

so that, after the substitutions of $P(s)$ and $Q(s)$, the Laplace domain solution for $\bar{c}_O(0, s)$ appears to be

$$\bar{c}_O(0, s) = s^{-1}c_O^* + \left[\frac{K_A}{K_A + 1} s^{1/2} - \frac{1}{K_A + 1} \frac{D_A}{D_O} (s+k)^{-1/2} \right] \frac{\bar{j}_F(s)}{nFD_M^{1/2}} \quad (\text{AII.15})$$

In the formulae of Section 5.6 the quotient D_A/D_O and the similar quotient D_B/D_R in the expressions for the R-component have been omitted, as usual. Evidently these factors can be incorporated by an alternative definition of the impedance Z_G .

List of Symbols

A	Electrode surface area (cm^2)
C_a	Adsorption capacitance (cf. Eq. (151b))
C_d	Differential double-layer capacitance (F cm^{-2})
C_{HF}	High frequency capacitance $= (\partial q / \partial E)_{\Gamma_O + \Gamma_R}$ (cf. Eq. (144b))
C_{LF}	Low frequency capacitance $= dq / dE$ (cf. Eq. (144a))
D	Diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
E	Electrode potential (V vs. reference electrode)
E°	Formal standard potential
$E_{1/2}$	Half-wave potential
$E_{1/2}^r$	"Reversible" half-wave potential $= E^\circ + (RT/nF) \ln (D_R/D_O)^{1/2}$
F	Faraday's constant, 96,500 coul mole $^{-1}$
$\tilde{F}$	$= (\partial j_F / \partial \phi)_{\text{CO,CR}}$
$F(t)$	Correction factor for d.c. nonreversible behavior (Eq. (45))
$H(t), H'(t)$	Idem for the d.c. interfacial concentrations (Eq. (42))
I	Electrical current intensity (amp)
I_F	Faradaic current intensity
I_C	Charging current intensity
K	Equilibrium constant
R	Gas constant
R_a	Charge transfer resistance for reaction via adsorbed species (cf. Eq. (150a))
R_{ct}	Charge transfer resistance ($\Omega \text{ cm}^2$), cf. Eq. (32)
R_Ω	Ohmic cell resistance
T	Absolute temperature ($^\circ\text{K}$)
V	Voltage (V)
Y	Complex admittance ($\Omega^{-1} \text{ cm}^{-2}$), $Y = Y' + iY''$
Y_{el}	Complex interfacial electrode admittance
Z	Complex impedance ($\Omega \text{ cm}^2$), $Z = Z' - iZ''$
Z_a	Adsorption impedance, cf. Eq. (155)
Z_F	Faradaic impedance
Z_C	Double layer impedance
Z_G	Gerischer impedance for mass transfer by a homogeneous reaction
$Z(s)$	Operational impedance (cf. Eq. (58))
Z_W	Warburg impedance for mass transfer by diffusion
$\widetilde{FF}, \widetilde{OF}$, etc.	Partial derivatives defined in Table 5
$\mathcal{L}$	Laplace operator
a_O, a_R	$D_O/\delta_O, D_R/\delta_R$, cf. Tables 3 and 14
b_O, b_R	$(K_A k_A^{1/2})^{-1}, (K_B k_B^{1/2})^{-1}$, cf. Table 14
c	Concentration

c'	d.c. interfacial concentration
c^*	Bulk concentration
c_O, c_R	Concentration of Ox and Red components, respectively
f	Frequency
g	k_A/ω , for homogeneous reaction preceding reduction
h	k_B/ω , for homogeneous reaction following reduction cf. Eq. (157)
i	Imaginary unit, $i = \sqrt{-1}$
j	Current density (Amp cm^{-2}), $= I/A$
j_F	Faradaic current density
j'_F	d.c. Faradaic current density
j_C	Charging current density
$\bar{k}, \tilde{k}$	Forward and backward rate constant of homogeneous chemical reaction
k	$\bar{k} + \tilde{k}$
k_f, k_b	Forward and backward rate constant of charge transfer reaction
k_{sh}	Standard heterogeneous rate constant $= k_f (E = E^\circ)$
l_1, l_2	Lorenz' partial charge transfer coefficients, cf. Eq. (128)
n	Total number of electrons transferred in the reaction $O \rightleftharpoons R$
p'	Irreversibility quotient, equal to R_{ct}/σ , or $2^{1/2}/\lambda$
p	$p' \omega^{1/2}$
q	Electrode charge density (coul cm^{-2})
q^*	$= q + nF\Gamma_O$
r_0	Radius of curvature of spherical electrode
s	The Laplace parameter (s^{-1})
t	Time (s)
u	$= (2\omega)^{1/2} \partial(\Gamma_O + \Gamma_R)/\partial\psi$
v	Reaction rate
x	Distance from electrode surface (cm)
y	Correction parameter for sphericity, cf. Eq. (34), $y = \pm \omega^{-1/2} (2D)^{1/2} / r_0$
α	Operational cathodic transfer coefficient, $= -(RT/nF) d \ln k_f / dE$
β_O, β_R	Adsorption coefficients
$\tilde{\gamma}$	Operator relating interfacial concentration and faradaic current, cf. Eq. (75)
Γ_i	Surface excess of component i (mole cm^{-2})
Γ	$\Gamma_O + \Gamma_R$
γ_ψ	$= (\partial\Gamma/\partial\psi)_E$
δ_O, δ_R	Thickness of diffusion layer, cf. Table 3
ε	$= (nF/RT) \Delta E$
ζ	$= (nF/RT) (E - E_{1/2}^\circ)$
θ	Fractional surface coverage

λ_i	$-\nu_i^*(nFD_i^{1/2})^{-1}\partial_{iF}/\partial c_i$ with $i = O, R, \dots$
λ	$= \lambda_O - \lambda_R$, equal to $k_f[\exp(\xi) + 1]D_O^{-1/2}$ in ART (Butler-Volmer) theory. See also Table 9
μ	Correction parameter for bounded diffusion, cf. Eq. (36) $\mu = \omega^{1/2} \delta / (2D)^{1/2}$
ν_i	Microscopic stoichiometric number
ν_i^*	Macroscopic stoichiometric number
ξ_O, ξ_R	$= D_O^{1/2}/r_O, D_R^{1/2}/r_O$, respectively
σ	The Warburg coefficient, $\sigma = \sigma_O + \sigma_R$
σ_O, σ_R	Separate Warburg coefficients for O and R
φ	$= (nF/RT)(E - E^\circ)$
ϕ	Phase angle
χ_ψ	$= \partial(q + nF\Gamma_O)/\partial\psi$ at constant E
ψ	Reinmuth's function, $c_OD_O^{1/2} + c_RD_R^{1/2}$
Ψ	Factor defined for large amplitude a.c. electrolysis, cf. Eq. (57)

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5

Rotating Disk and Ring-Disk Electrodes

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Notation

A list of symbols used in this chapter with their definitions can be found on page 349.

1. Introduction

The use of the rotating disk electrode (RDE) is one of the main techniques in modern experimental electrochemistry. Favorable methodological features, e.g., the comparative simplicity of the technique in combination with high accuracy, the availability of a rigorous quantitative theory, and the possibility of conducting experiments in a stationary kinetic regime, make this method one of the most fruitful means of investigating the kinetics and mechanisms of electrode processes.

In studying electrochemical reactions, it is, in most cases, essential to separate the processes occurring on the electrode surface from those affecting the transport of the reagents and the reaction products. Electrochemical measurements in agitated solutions, in principle, allow a quantitative description of the mass transfer stage and permit correction for it during analysis of the kinetics of heterogeneous conversion proper. In practice, however, it is only possible to describe the influence of mass transfer in some rare cases

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where the pattern of the movement of the solution near the electrode can be described with sufficient accuracy.

The rotating disk electrode (RDE) technique was discovered as a result of applying the concepts of theoretical hydrodynamics to the analysis of electrochemical problems. In 1942, by examining convective diffusion in moving media, Levich⁽¹⁾ showed that an electrode in the form of a rotating disk exhibits a unique combination of certain factors: the possibility of exact calculation of the diffusion flow, the uniform accessibility of the surface with respect to diffusion, and a steady state regime (unlike, say, the dropping mercury electrode). These advantages naturally suggested that the rotating disk electrode would be a promising tool for electrochemical investigations.

Soon after the publication of the first theoretical paper, Siver and Kabanov⁽²⁾ succeeded in using the RDE method experimentally and demonstrated that the limiting diffusion current calculated is in good agreement with experiment. Subsequent experimental verification of the main principles of the RDE method has fully revealed its advantages. Gradually more and more problems were resolved using the RDE method. In the fifties, no more than 10–15 experimental papers reporting the results obtained by the RDE method were published every year, but by the seventies approximately 100–200 publications were reporting results obtained by using the RDE method, or one of its modifications. The method has been applied to the mechanism and kinetic characteristics of electrode reactions, to study of homogeneous chemical reactions involved in electrochemical processes, and to measuring the diffusion coefficients and the concentrations of solutes. The technique is widely used in electroanalytical chemistry since a variety of electrode reactions taking place in a wide potential range may be studied for analytical purposes.

It would be appropriate to note that until the middle of the forties, theoretical electrochemistry developed primarily as the electrochemistry of the mercury electrode. The discovery of the RDE method served as a stimulus for investigating solid electrodes which are important both from a theoretical and a practical viewpoint, and it provided an opportunity to extend the range of study further into the anode potential region. Compared with the dropping mercury electrode, the most common technique then used, the RDE has one essential advantage: the possibility of conducting measurements at considerably higher electrochemical reaction rates.

The potentialities of the RDE were widened still further after the invention of the rotating ring-disk electrode (RRDE), an important modification of the technique first suggested by Frumkin and Nekrasov⁽³⁾ in 1959. The first quantitative theory of the rotating ring-disk electrode was proposed by Levich and Ivanov.^(4,5) In the subsequent papers, Albery, Bruckenstein *et al.* made exact calculations of the main characteristic parameter of the technique, i.e., the collection efficiency of the RRDE, defined as the fraction of an intermediate generated at the disk that is collected at the concentric ring. The latter is separated from the disk by an insulator. These authors suggested ways of

utilizing the RRDE in investigating a number of electrochemical kinetic problems. The possibility of separating and independently analyzing electrochemical reaction intermediates is a unique and inherent feature of the technique. It is especially helpful in studying complicated multistage reactions, for example, in organic electrochemistry, in anodic dissolution of metals, and in other similar cases. An important practical application of the RRDE method is in the study of oxygen reduction reactions. The results obtained, using this method, on the electrocatalytic properties of carbon and group VIII metals have been extensively used in designing oxygen electrodes for fuel cells.

A number of monographs and reviews are devoted to the RDE and RRDE techniques.⁽⁵⁻¹¹⁾ In this chapter, the basic principles of the theory and technique of RDE and RRDE will be presented; they will be illustrated by typical experimental results. A detailed account of the methods can be found in our monograph⁽⁷⁾ to which frequent reference will be made.

2. Hydrodynamics

The flow of a viscous incompressible liquid due to a disk of large diameter rotating at a constant speed is rather complex. Owing to the action of viscous forces, the liquid layers adjacent to the disk surface are also involved in motion along with the disk. The rotational motion, however, gradually decreases as the distance from the disk surface increases. The centrifugal forces arising in rotational motion throw the liquid outwards from the axis of rotation to the disk periphery, and displaced liquid is replaced by that from the bulk. A constant flow of liquid along the axis to the rotating surface arises at a considerable distance from the disk surface (Figure 1a). On the whole, the resulting pattern of liquid flow resembles the motion of air in the vicinity of a rotating fan. A three-dimensional representation of this flow is shown in Figure 1b.

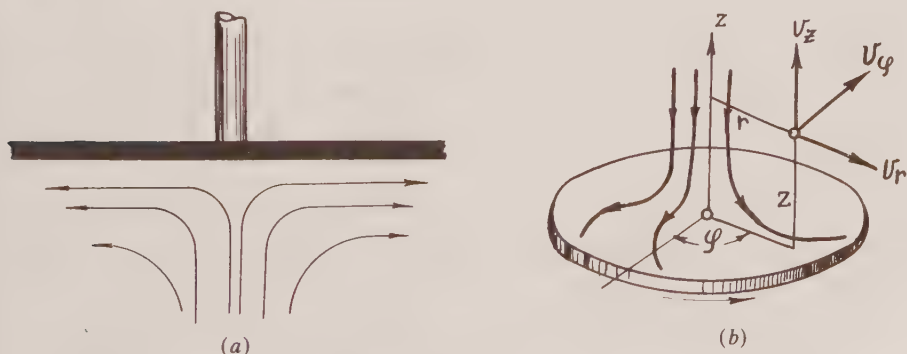


Figure 1. Hydrodynamics of a rotating disk: (a) streamlines in solution; (b) coordinate system used in calculation (solid lines denote streamlines).

A theoretical description of the liquid motion near an infinitely large disk rotating at a constant angular velocity, ω , is one of the classical problems in hydrodynamics (the so-called Karman problem). Where laminar flow occurs, this problem reduces to equations which can be integrated without any significant constraints. Such integration was first attempted by Karman,⁽¹²⁾ using a special approximate calculation method. Subsequently, Cochran⁽¹³⁾ made an exact calculation of the velocity distribution by numerical integration. More recently, computers have been successfully applied to study various aspects of the Karman problem. The present state of the investigation of rotating disk hydrodynamics has been outlined in the monograph by Dorfman,⁽¹⁴⁾ and in recently published reviews.⁽¹⁵⁻¹⁶⁾ Here, we shall give the essential results of these calculations.

To describe the flow of a medium in the vicinity of a rotating disk, it is convenient to use the cylindrical coordinates, r , ϕ , and z (Figure 1b), due to the axial symmetry of the system under consideration. Let v_r , v_ϕ and v_z denote the components of the liquid velocity, $\mathbf{v}$, in the radial, azimuthal, and axial directions, respectively. Karman⁽¹²⁾ has shown that for a uniform rotational motion of an infinitely large disk, the distribution patterns of v_r , v_ϕ and v_z have certain interesting features. First, he established that the motion of the liquid toward the disk surface (v_z) proceeds at a constant rate, irrespective of the distance from the rotational axis. Second, there is a similarity in the distributions of the components, v_r and v_ϕ , at different distances from the rotational axis. The components, v_r , v_ϕ , and v_z , depend on the variables r and z as follows:

$$v_r = r\omega F(\zeta), \quad v_\phi = r\omega G(\zeta), \quad v_z = (\eta_0\omega)^{1/2}H(\zeta), \quad (1)$$

where

$$\zeta = z(\omega/\eta_0)^{1/2} \quad (2)$$

η_0 is the kinematic viscosity of the liquid, and ω is the angular velocity of the disk.

Calculation of the functions, F , G , and H , represents the main task in solving the Karman problem. The following boundary conditions, which have simple physical meanings, may be used in calculating these functions.

The liquid layers adjacent to the disk surface rotate along with the disk; therefore:

$$v_r = 0, \quad v_\phi = r\omega, \quad v_z = 0 \quad (\text{or } F = 0, G = 1, H = 0) \quad \text{for } \zeta = 0 \quad (3)$$

At a remote distance from the disk surface, rotational motion ceases, so that:

$$v_r \rightarrow 0, \quad v_\phi \rightarrow 0 \quad (\text{or } F \rightarrow 0, G \rightarrow 0) \quad \text{as } \zeta \rightarrow \infty. \quad (4)$$

By analyzing the equations of liquid motion in the vicinity of a rotating disk under the above boundary conditions, Cochran⁽¹³⁾ derived the following

asymptotic representation for the functions, F , G , and H , in the vicinity of the disk surface and remote from it.

In the vicinity of the disk surface (for $\zeta \ll 1$):

$$\begin{aligned} F &= a_0 \zeta - (\zeta^2/2) - (b_0 \zeta^3/3) - (b_0^2 \zeta^4/12) - \dots \\ G &= 1 + b_0 \zeta + (a_0 \zeta^3/3) + [(a_0 b_0 - 1) \zeta^4/12] - \dots \\ H &= -a_0 \zeta^2 + (\zeta^3/3) + (b_0 \zeta^4/6) + \dots \end{aligned} \quad (5)$$

At a remote distance from the disk surface ($\zeta \gg 1$):

$$\begin{aligned} F &= A_0 \exp(-C_0 \zeta) + [B_0(A_0^2 + B_0^2)/2C_0^2] \exp(-2C_0 \zeta) + \dots \\ G &= B_0 \exp(-C_0 \zeta) - [B_0(A_0^2 + B_0^2)/12C_0^3] \exp(-3C_0 \zeta) + \dots \\ H &= -C_0 + (2A_0/C_0) \exp(-C_0 \zeta) - [(A_0^2 + B_0^2)/2C_0^3] \exp(-2C_0 \zeta) + \dots \end{aligned} \quad (6)$$

According to numerical calculation,⁽¹⁷⁾ the constants, A_0 , B_0 , C_0 , a_0 , and b_0 , have the following values:

$$\begin{aligned} A_0 &= 0.91772; & B_0 &= 1.20211; & C_0 &= 0.88446; \\ a_0 &= 0.510233; & b_0 &= -0.61592 \end{aligned} \quad (7)$$

The behavior of the functions, F , G , and H , in the entire range of variation of the variable, ζ , is shown in Figure 2.

From these plots it is seen that the azimuthal component of the liquid velocity decreases rapidly as the distance from the disk surface increases. At a distance, $\zeta = 3.6$, the value of the function $G(\zeta)$ is only 5% of the corresponding value at the disk surface. Therefore, a layer of thickness:

$$\delta_0 = 3.6(\eta_0/\omega)^{1/2} \quad (8)$$

shall be referred to as the hydrodynamic boundary layer at the rotating disk. From Eq. (8) it is evident that δ_0 decreases as the rotation velocity increases, and is not dependent on the distance from the rotational axis. This latter feature is very important for mass transfer and consequent physicochemical applications.

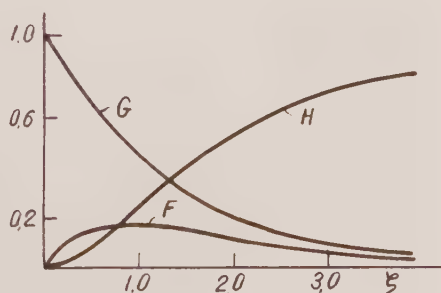


Figure 2. Distribution of velocity components near a disk rotating in an immobile liquid⁽¹³⁾. F , G , and $|H|$ represent the radial, azimuthal, and axial components, respectively [Eq. (5)].

All the above results were derived for a disk of infinite size. Under certain conditions, the basic theoretical conclusions on the flow pattern can also be applied to a disk of finite radius, r_0 . Obviously, radius r_0 should be sufficiently large for the edge of the disk to have no perceptible influence on flow. This is attained if $r_0 \gg \delta_0$. However, radius r_0 cannot be greater than a certain critical value, since an increase in r_0 above this critical value will lead to disruption of laminar flow. The liquid flow will then acquire an entirely different pattern: it becomes unstable, and turbulent flow results. Random perturbations of this type of flow, caused by various factors, are not damped as in the case of laminar flow but are spontaneously intensified and innumerable random vortices appear in the flow direction. A similar effect occurs with excessive increase in rotation speed. If we use the dimensionless Reynolds number parameter, $Re = \omega r_0^2 / \eta_0$, then laminar flow becomes unstable at Re greater than some critical value Re_{crit} . The magnitude of Re_{crit} depends on many factors, and has been reported differently in papers by various authors. In all probability, transition from laminar flow to turbulent flow may be assumed to take place in the range of Reynolds number from 1.5×10^5 to 3.1×10^5 [References (14–18)]. At higher Reynolds numbers, flow becomes completely turbulent.

At present, the theoretical description of turbulent flow caused by the motion of solids in liquids is based on conventional models based on the additional transfer of momentum due to turbulent fluctuations. One of the most common models in the theory of turbulent boundary layers is the hypothesis of effective viscosity due to turbulent fluctuations. Cooper⁽¹⁹⁾ has calculated the distribution of the averaged velocity components of a liquid in the vicinity of a rotating disk in turbulent flow. It should, however, be emphasized that turbulent flow near a rotating disk has not as yet been described theoretically in a satisfactory manner. The nature of turbulent flow seems to be highly sensitive to the design features of the experimental equipment. Therefore, laminar flow is most often used in the practical applications of rotating disk electrodes, despite the increase in mass transfer rate occurring with turbulent flow.

3. Convective Diffusion

The flow of electric current through an electrochemical cell is associated with the transfer of the components of solution.^(5,7,9) Besides the mechanical motion of the electrolyte as a whole, the causes of the motion of ionic components are the external forces (in the first instance, electrical forces) and the concentration gradients. In the case of dilute electrolyte solutions, the flow of each of the dissolved components is described by the equation:

$$J_i = \mathbf{v}c_i - D_i \text{grad } c_i + z_i F \lambda_i c_i \text{grad } \Phi \quad (9)$$

where c_i is the concentration of the i th component, D_i is the coefficient of molecular diffusion, λ_i is the mobility, z_i is the charge per mole of the i th type particles, Φ is the potential of the electric field in the solution, and $\mathbf{v}$ is the rate of motion of the solution. In addition, if there is a gradient of temperature, pressure, or any other external force in the cell, certain supplementary terms may have to be included in Eq. (9) because these factors may further affect the displacement of the solution components.

If no mutual chemical transformations between components take place in the cell, then for each type of particle we may write the following equation for material balance:

$$\mathbf{v} \cdot \text{grad } c_i = \text{div} (D_i \text{ grad } c_i - z_i F \lambda_i c_i \text{ grad } \Phi) \quad (10)$$

With the exception of the region of the electrical double layer near the electrode surface, which extends to a distance of 10^{-7} – 10^{-6} cm for moderate electrolyte concentrations, the solution in the cell is electrically neutral, i.e.,

$$\sum_i z_i F_i c_i = 0 \quad (11)$$

Equations (10) and (11) form a system which can be used to describe the distribution of solution components, c_i , and of the electric field, Φ , in the cell.

The transport equations (10) and (11) must be supplemented with the boundary conditions at the electrodes and at the cell walls generally. The boundary conditions characterize the nature of the electrochemical transformations and their rates. They, therefore, have considerable influence on the distribution of ion concentrations and of the electric field in the cell.

A theoretical description of the motion of the solution components becomes more complicated on increasing the reagent concentration. In concentrated solution, the gradient of component activity is the motive force of diffusion, while the transport coefficients (e.g., viscosity, diffusion coefficient, etc.) are functions of solution composition and concentrations. Consequently, more general relationships for partial flows⁽⁹⁾ have to be used in place of Eq. (9).

Moreover, in concentrated solutions the momentum transferred by the ionic components of the solution forms a perceptible part of the liquid's total momentum. Hence, the solution flow pattern depends on the magnitude of current passing through the solution. The distribution of the liquid velocity, $\mathbf{v}$, can only be determined by solving the hydrodynamic problem and the convective mass transfer problem simultaneously.⁽²⁰⁾

The pattern of ionic mass transfer is greatly simplified if the electron transfer process is carried out in the presence of an indifferent electrolyte. The indifferent electrolyte, when added in excess, improves the conductivity of the solution and decreases the internal resistance of the cell. In this case, the effect of the electric field on the transport of electrochemically active ions may be neglected. To describe the convective diffusion of electroactive

components, a simplified transport equation (10) may then be used. Neglecting the effect of the electric field on mass transfer, we can write the equation as:

$$\mathbf{v} \text{ grad } c_i = D_i \Delta c_i \quad (10a)$$

This equation coincides with the equation of convective diffusion of uncharged particles.

An analysis of the individual terms in Eq. (10a) shows that one part of the terms is often considerably less than the others. Thus, for example, in convective mass transfer to the surface of a rotating disk, the main change in the concentration of the transported component is confined to a relatively narrow layer of solution near the disk surface. For the majority of liquids under diffusion conditions, this layer is about 10^{-3} – 10^{-4} cm for moderate rotation velocities of the disk. Diffusion mass transfer in the radial direction is unimportant, and thus, Eq. (10a) may be simplified:

$$v_r \frac{\partial c}{\partial r} + \frac{v_\phi}{r} \frac{\partial c}{\partial \phi} + v_z \frac{\partial c}{\partial z} = D \frac{\partial^2 c}{\partial z^2} \quad (12)$$

The components of the liquid velocity, v_r , v_ϕ , and v_z , may then be determined from Eq. (1).

Let us suppose that the rate of transformation of the reactant is the same at all points on the surface of the rotating disk (in other words, the surface has a uniform catalytic activity). As a consequence of the reaction, a certain concentration of the substance is established near the disk surface:

$$c = c_s \quad (\text{for } z = 0, r \geq 0) \quad (13a)$$

which differs from the bulk value:

$$c = c^* \quad (\text{for } z \rightarrow \infty) \quad (13b)$$

In the case under consideration, the concentration distribution of matter transported does not depend on the variables, r and ϕ , and can be found by integrating the equation:

$$v_z \frac{dc}{dz} = D \frac{d^2 c}{dz^2} \quad (14)$$

It can be easily shown that the solution of Eq. (14) under the boundary conditions (13a) and (13b) is:

$$c = c^* - (c^* - c_s) \times \left\{ 1 - \left[\int_0^z \exp\left(\frac{1}{D} \int_0^{z'} v_z(z'') dz''\right) dz' \right] / \left[\int_0^\infty \exp\left(\frac{1}{D} \int_0^{z'} v_z(z'') dz''\right) dz' \right] \right\} \quad (15)$$

In calculating the integrals contained in Eq. (15), generally speaking, we have to use the axial component of the liquid velocity, $v_z(z)$, throughout the entire range of variation of the argument. However, in early calculations,⁽¹⁾ it was assumed that $v_z(z)$ could be represented in the form:

$$v_z \approx -a_0 \omega^{3/2} \eta_0^{-1/2} z^2 \quad (\text{for } z \rightarrow 0) \quad (16a)$$

$$v_z \approx -C_0 \omega^{1/2} \eta_0^{1/2} \quad (\text{for } z \rightarrow \infty) \quad (16b)$$

These equations follow directly from the asymptotic representations (5) and (6).

After integration, we obtain the following expression for the concentration distribution of the diffusing material near the rotating disk:

$$c = c^* - (c^* - c_s) \{1 - \gamma[1/3; a_0 \omega^{3/2} z^3 / (3D\eta_0^{1/2})] / \Gamma(1/3)\} \quad (17)$$

where $\gamma[1/3; a_0 \omega^{3/2} z^3 / (3D\eta_0^{1/2})]$ is the incomplete gamma-function of the arguments.⁽²¹⁾

The concentration distribution corresponding to Eq. (17) is shown in Figure 3. It is easily seen [in agreement with direct calculations using Eq. (17)] that already at a distance:

$$\delta_d = 1.61 D^{1/3} \eta_0^{1/6} \omega^{-1/2} \quad (18)$$

from the disk surface the concentration of the transported matter differs from the bulk value only by 0.5%. The quantity, δ_d , is called the thickness of the diffusion boundary layer at the rotating disk. For convective diffusion in water and in dilute aqueous solutions, for which $Sc = \eta_0 / D \sim 10^3$, the thickness δ_d at a rotation velocity of 10 rpm is equal to 0.005 cm. For this same rotation velocity, the thickness of the hydrodynamic boundary layer δ_0 , according to Eq. (8), is about 0.11 cm, i.e., almost 20-fold greater. Clearly, the large ratio between δ_0 and δ_d justifies approximations (16a) and (16b) assumed in describing $v_z(z)$.

From Eq. (18) it follows that the thickness is the same over the entire surface of the disk. There are two reasons for this property of uniform

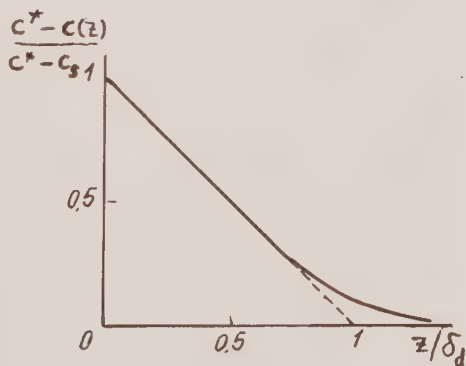


Figure 3. Concentration distribution near a rotating disk.

accessibility to diffusion: first, the specific hydrodynamics inherent in a rotating disk, and second, the assumption that the electrocatalytic activity of the electrode surface is uniform [boundary condition (13a)]. Violation of any one of these conditions will imply the loss of uniform accessibility to diffusion.

As already mentioned, uniform accessibility to diffusion is a very rare property among the various systems with forced convection. This is a distinguishing feature of the rotating disk among other hydrodynamic systems, and notably simplifies the consideration of mass transfer to its surface.

The density of the convective flow to the rotating disk surface is calculated from Eq. (17):

$$j = D(dc/dz)_s = D(c^* - c_s)/\delta_d \quad (19)$$

and δ_d is determined with the help of Eq. (18).

If the electrochemical reaction at the disk surface is accompanied by the transfer of n electrons, the electric current density at the RDE i is equal to:

$$i = nFj = nFD(c^* - c_s)/\delta_d = 0.62nF(c^* - c_s)D^{2/3}\eta_0^{-1/6}\omega^{1/2} \quad (20)$$

The total current I at a disk electrode of radius r_0 is obtained on multiplying Eq. (20) by the disk area, S :

$$I = nFD(c^* - c_s)S/\delta_d = nFD(c^* - c_s)\pi r_0^2/\delta_d \quad (21)$$

A maximum rate of mass transfer is observed in rapid heterogeneous reactions, when all the substance transferred to the disk surface is instantly converted. The density of the limiting diffusion flux for this case is obtained from Eq. (19) by taking $c_s = 0$:

$$j = Dc^*/\delta_d \quad (22)$$

The density of the limiting diffusion current is derived analogously from Eq. (20):

$$i_d = 0.62nFc^*D^{2/3}\eta_0^{-1/6}\omega^{1/2} \quad (23)$$

From Eq. (23) it is evident that i_d is proportional to $\omega^{1/2}$. This functional dependence is one of the main criteria in using rotating disk electrodes.

In the preceding pages, account was taken only of the first term (proportional to z^2) in the expansion [Eq. (16a)] of the axial component of the liquid velocity in calculating the concentration distribution for the transported substance. As already mentioned, such an approximation is justified for a sufficiently high Schmidt number $Sc = \eta_0/D$ ($Sc > 10^3$). A more exact representation of the function $v_z(z)$ must be used in calculating the diffusion current more accurately. In particular, we may take into account (cf. Gregory and Riddiford⁽²²⁾) the next term (proportional to z^3) in the expansion of $v_z(z)$. Gregory and Riddiford⁽²²⁾ obtained the following expression for the limiting diffusion current density:

$$i_{dR} = 0.621nFc^*D^{2/3}\eta_0^{-1/6}\omega^{1/2}[1 + 0.3539(D/\eta_0)^{0.36}]^{-1} \quad (23a)$$

Newman⁽²³⁾ has given an even more accurate account of liquid motion in a direction normal to the disk surface. The limiting diffusion current, thus calculated, can be represented in the form:

$$i_{dN} = 0.621 n F c^* D^{2/3} \eta_0^{-1/6} \omega^{1/2} \times [1 + 0.2980(D/\eta_0)^{1/3} + 0.14514(D/\eta_0)^{2/3}]^{-1} \quad (23b)$$

In Newman's view, this equation gives an i_d value for $Sc > 100$, differing by less than 0.1% from that obtained by numerical integration of the convective diffusion equation.

The discrepancy between the approximate (Eq. 23) and more exact [Eqs. (23a), (23b)] expressions depends on the value of the Schmidt number. For $Sc \geq 10^3$, it does not exceed 3%, and for lesser Sc , the discrepancy may reach 15–20%.

It should, however, be emphasized that a more exact account of the influence of the solution motion at lesser Schmidt numbers does not alter the functional dependence of the diffusion current on $\omega^{1/2}$.

In considering the convective diffusion to the rotating disk surface, we assumed that the electrode surface has uniform activity with respect to heterogeneous reactions. In actual practice, various contaminations, oxide traces, projections of different crystallographic faces, etc., make the surface nonhomogeneous: the electrochemical reaction rate may prove to be different in different regions of the surface. If the areas of constant activity are comparable in dimensions with δ_d (i.e., the characteristic size of the heterogeneity region is 10^{-3} – 10^{-4} cm), then the heterogeneity of the surface of the RDE will distort the pattern of mass transfer. Instead of a uniform distribution of flow of the electroactive reagent to the electrode surface ($\partial j_d / \partial r = 0$), we would expect an increase in the diffusion flow density near the active regions, while considerably lesser amounts of the reagent will be transferred to the less active regions. The rotating disk surface then loses its property of uniform accessibility to diffusion.

Landsberg and Thiele⁽²⁴⁾ have proposed a model for calculating the limiting current i_d at a macroscopically non-uniform RDE. The model is very approximate and has been discussed in detail in Reference (10). One of the authors⁽²⁵⁾ has re-examined this problem from a different viewpoint.

4. Migration and Distribution of the Electric Field

We shall briefly outline the part played by the electric field in a cell with an RDE [detailed information on this topic can be found, for example, in References (5), (7) and (9)]. We shall assume that the counter electrode in the cell is sufficiently large, so that electrochemical processes taking place on its surface may be disregarded. The total overpotential, η , under the current

flow can be divided into several components: the overpotential η_s developed at the electrode/electrolyte interface, the concentration overpotential η_c , and the ohmic potential drop, Φ_0 :

$$\eta = \eta_s + \eta_c + \Phi_0 \quad (24)$$

The "surface" overpotential η_s depends on the specific features of the charge kinetics at the electrode/electrolyte interface for the particular electrochemical process. The concentration overpotential η_c characterizes the potential drop inside the cell in the region near the electrode surface where the concentration of the ionic components of the solution changes. In the region of constant concentration, the potential drop Φ_0 inside the cell is of purely ohmic nature. The relative role of the terms in Eq. (24) depends on the local value of the current density at the electrode, and also on the solution composition, kinetics of the electrode process, and on the geometrical dimensions of the cell. We shall, therefore, restrict ourselves to consideration of the simplest limiting cases.

The ohmic potential drop Φ_0 in the electrochemical cell with excess indifferent electrolyte described above is unimportant as compared to η_c and η_s , due to the high conductivity of the solution. Here the limiting stages in the current formation process are the transport of the reagent and the electrochemical reaction proper at the electrode. Since the indifferent electrolyte does not participate directly in the electrode process, the electric field has hardly any effect on the transfer of charged components in the diffusion boundary layer δ_d either, where the concentration changes in a sufficiently strong manner. To describe the distribution of the reagents in the vicinity of an RDE, we can, therefore, use the equations for convective diffusion of neutral species (Eq. 14), as discussed earlier. The current density at an RDE with uniform electrochemical activity is the same at all points on the electrode surface. Under conditions of slow electrochemical discharge, it will be described by Eq. (41) (see below, Section 6).

With lower concentrations of indifferent electrolyte, the electric field begins to play an increasing part in the reagent transfer process. In particular, migration of ions under the action of an electric field⁽⁹⁾ has a significant influence in the diffusion boundary layer δ_d . In a binary electrolyte solution, i.e., a solution containing only two types of ions, the limiting current i_{lim} , due to diffusion and migration, is far greater than the limiting *diffusion* current under the same conditions. As demonstrated in Reference 5, calculation of the electric current in a binary electrolyte again formally leads to the equation of convective diffusion for neutral particles (Eq. 14). The diffusion coefficient D in this case, however, takes the value of the effective diffusion coefficient of the solution:

$$D_{\text{eff}} = \frac{z_+ D_- - z_- D_+}{z_+ - z_-} \quad (25)$$

where z_+ , D_+ , z_- , D_- are the charge and the diffusion coefficient of the cation

and anion, respectively. The following expression has been derived for the current density at the RDE:

$$i_{\text{lim}} = i_{d+}/(1 - t_+) = z_+ F D_{\text{eff}} c_+^* / \delta_d (1 - t_+) \quad (26)$$

where $t_+ = z_+ / (z_+ - z_-)$ is the cation transfer number, and c_+^* is the concentration of cations in the bulk of the solution. The thickness of the diffusion boundary layer δ_d may be calculated from Eq. (18), using the effective diffusion coefficient (Eq. 25).

All the preceding arguments, strictly speaking, relate to the limiting current case where the concentration of ions which discharge on the electrode surface is almost zero. The distribution of current on the RDE surface in this case is homogeneous, i.e., the local current density does not depend on the distance from the center of the disk.

Another limiting case is represented by the electrochemical systems in which the concentration variations in the solution caused by the current passing through the cell may be neglected. This case occurs if a current which is small in comparison to the limiting diffusion current I_d flows through the cell. Under these conditions, the concentration overpotential η_c is far less than both η_s and Φ_0 . The potential drop in the cell is then purely of ohmic nature.

It is readily seen that the electric field distribution in the cell is described by the Laplace equation:

$$\Delta \Phi_0 = 0 \quad (27)$$

which is derived from Eq. (10) for $c_i \equiv \text{const.}$

As a consequence of the axial symmetry of a cell with a disk electrode, Eq. (27) takes the form:

$$\frac{\partial^2 \Phi_0}{\partial r^2} + \frac{1}{r} \frac{\partial \Phi_0}{\partial r} + \frac{\partial^2 \Phi_0}{\partial z^2} = 0 \quad (28)$$

At a point remote from the electrode, the equilibrium potential distribution is preserved, and, therefore:

$$\Phi_0 \rightarrow 0 \quad \text{for } z \rightarrow \infty, r \geq 0 \quad (29)$$

(Indeed, this condition should be specified for large but finite z .)

In real systems, a disk electrode is often represented as a disk of radius r_0 made of metal or any other conducting material located at the center of a large insulating disk (see Section 5.1a). Then, outside the limits of the electrode area:

$$(\partial \Phi_0 / \partial z)_s = 0 \quad \text{for } z = 0, r > r_0 \quad (30)$$

Depending on the nature of the electrochemical process taking place on the electrode surface, various limiting cases may occur:

(a) for nonpolarizable electrodes, when there is no surface overpotential:

$$\Phi_{0s} = \eta \quad \text{for } z = 0, r \leq r_0 \quad (31a)$$

i.e., the cell voltage is completely expended in ohmic losses;

(b) for a "weakly polarizable" electrode, we can assume that the kinetics of the electrochemical reaction may be described by a linear relationship, thus:

$$-\kappa(\partial\Phi_0/\partial z)_s = k(\eta - \Phi_{0s}) \quad \text{for } z = 0, r \leq r_0 \quad (31b)$$

where k is a certain constant, and κ is the conductivity of the solution;

(c) for processes occurring with high surface overpotential, it may be assumed that η_s is considerably greater than the other overpotential terms, and approaches the total overpotential η . Thus:

$$-\kappa(\partial\Phi_0/\partial z)_s = i = \text{const.} \quad \text{for } z = 0, r \leq r_0 \quad (31c)$$

Here i is the current density at the disk electrode.

The distributions of current and potential corresponding to the above three cases are treated in detail in References (7)–(9). In particular, the current distribution along a non-polarizable electrode is given by the expression:

$$i = 2\eta\kappa/\pi(r_0^2 - r^2)^{1/2} \quad (32)$$

Typical patterns of the electric potential distribution in a cell with a disk electrode are shown in Figure 4.⁽²⁶⁾

It should be emphasized that the three cases considered above relate to the simplest potential distributions in a cell with the RDE. Other more complicated cases of current flow patterns in such cells are examined in Reference (9).

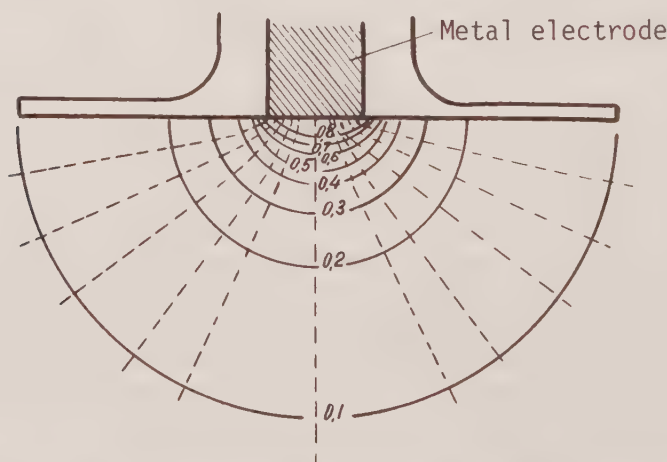


Figure 4. Potential distribution in solution near an RDE of finite radius enveloped by an insulating jacket. Broken lines denote streamlines, solid lines are equipotentials. Solution potential is taken to be zero and the RDE potential to be unity.

5. Applications of the RDE in Investigations of Diffusion

5.1. Choice of Experimental Conditions

The rotating disk electrode technique is extensively used in studying mass transfer and electrode kinetics (see below). As mentioned above, the most attractive feature of the RDE technique is the availability of a quantitative theory which makes it possible to determine the characteristic parameters both of diffusion and of the electrode reaction with high accuracy without the fundamental need for supplementary operations, e.g., calibration, etc. However, this situation implies that certain requirements need to be imposed on the experimental conditions used. The main purpose of these requirements is that the measurement conditions should be in complete agreement with the basic assumptions underlying the theoretical calculations. We shall state these conditions in brief.

(a) Laminar flow condition: As the rotation speed increases, turbulent flow is developed near the peripheral disk region, whereas flow continues to be laminar in the inner region. Transition to turbulent flow takes place on attaining a certain critical Reynolds number $Re = r_0^2 \omega / \eta_0$ (see p. 298). A convenient nomogram for the determination of Re_{crit} for a given r_0 and ω is presented in Reference 11. For a given disk radius the laminar flow condition can easily be maintained by controlling rotation speed. However, it should be remembered that factors such as the surface roughness, vibration of the electrode, etc., may give rise to turbulence even when $Re < Re_{crit}$.

Special constructional requirements are therefore needed for the shape of the insulating jacket around the electrode. This jacket not only protects the lateral electrode surface but also prevents turbulence in the direct vicinity of the disk perimeter where vortices may otherwise be developed due to unfavorable conditions of liquid flow around the rotating body. The lateral surface of the jacket in turn should only introduce the minimum amount of distortion into the liquid flow and this may be attained by giving the jacket a specialized profile. Experiments have shown that the concave conic shape presented in Figure 5 is optimal.⁽²⁷⁾ A simple cylindrical shape also gives satisfactory results.

(b) Suppression of migration and ohmic drop in the solution: This may be effected by adding excess amounts of an indifferent electrolyte to the solution so that the concentration of reagent is low compared with the total concentration of the electrolyte solution. Besides giving high conductivity, an excess of indifferent electrolyte creates conditions in which the diffusion coefficient of the reacting particles may be taken to be constant. In general, the diffusion coefficient depends on the solution concentration [for details see Reference (7)], since concentrations in the diffusion equation should strictly be replaced by activities.

(c) Choice of optimal electrode size and cell volume: The theory of a rotating disk electrode was developed for an infinite plane rotating in a

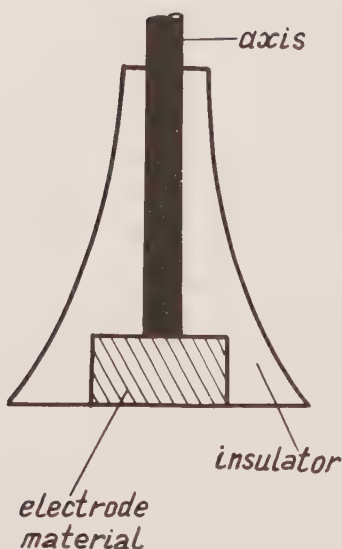


Figure 5. Optimal shape of insulating jacket.

semi-infinite volume of liquid. In reality, the electrode and the cell are limited in dimensions. The question therefore arises as to the extent that the quantitative theory of a rotating disk is applicable to experimental results obtained with a rotating electrode under real conditions.

Use of an electrode of finite radius naturally gives rise to the so-called edge effect. The effect results from diffusion to the peripheral disk regions taking place not only normal to the surface, but also in radial directions. As a result of this enhanced diffusion, the current density at the disk edges is higher than that calculated by means of Eq. (23) (see Figure 6).

The edge effect extends to a circular region on the disk surface, the width of this ring being of the order of the diffusion boundary layer thickness δ_d . It is, therefore, highly pronounced at low disk rotation speeds and on electrodes of small radius. Using theory derived for this effect,⁽²⁸⁾ and specifying the accuracy required, for a given D and η_0 , we may choose the radius of the disk and the range of the rotation speed so that the error due to the edge effect may be negligibly small.

As regards the limiting volume of the solution in the cell, experiments⁽²⁹⁾ have shown that the theory of the rotating disk electrode is still applicable to the measurements of the limiting diffusion current taken on disk of radius 2–3 mm in a cell of operating volume as low as 1 mL.

At low electrode rotation speed, at which forced stirring of the solution is not very great, a perceptible contribution to mass transfer is made by the natural convection due to the differences in the densities of the solution in different areas of the cell, temperature fluctuations, etc. The measured current then proves to be greater than the value calculated by the theory of convective

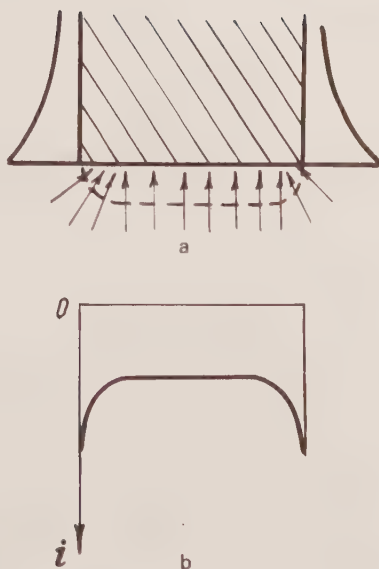


Figure 6. A scheme of the origin of edge effect (a) and current density distribution on an RDE surface (b).

diffusion. This effect imposes a lower limit on the operating range of rotation speed.

(e) The influence of mechanical defects: Such factors as eccentricity and vibration of the rotation electrode, and its surface roughness, do not exert considerable influence on mass transfer. Thus, if the eccentricity (i.e., the ratio of radial displacement of the electrode during rotation to the radius of the operating surface) does not exceed 0.5, then its influence on the limiting diffusion current may be disregarded.⁽³⁰⁾

5.2. Experimental Verification of the Theory

The first paper in which the RDE method was substantiated by experiment⁽²⁾ showed the existence of a characteristic relationship between the limiting current and the square root of the electrode rotation speed. A more rigorous verification of the theory presented above lies in comparing the calculated diffusion flux (or current) with the experimentally measured value. The values of the diffusion coefficient, viscosity, and other parameters needed in the calculations should be measured by an independent method with sufficient accuracy.

The most exact and systematic verification of the theory has been carried out by Riddiford and co-workers.⁽³¹⁾ As an example, Figure 7 shows the measured values of limiting current of reduction of the I_3^- ions on a platinum electrode (circles). The solid lines in this figure represent the curves calculated by Eq. (23a). In this experiment, the diffusion coefficient and the viscosity of the solution were varied by changing the temperature and by adding saccharose

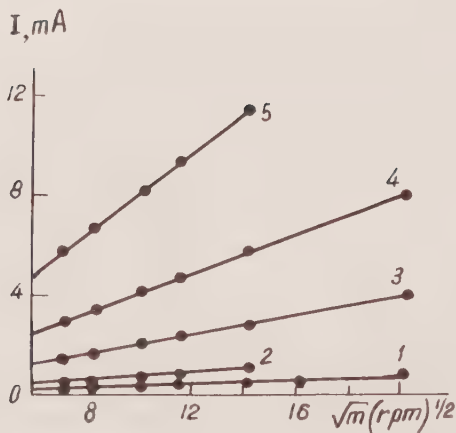


Figure 7. Verification of the RDE theory⁽³¹⁾; limiting current of reduction of I_3^- in 0.1 M KI solution vs. square root of the rotation speed. KI_3 concentration (mole/L); (1) 1.24×10^{-4} ; (2) 2.41×10^{-4} ; (3) 6.14×10^{-4} ; (4) 1.24×10^{-3} ; (5) 2.47×10^{-3} .

to the solution. The diffusion coefficient was determined by the method of nonstationary diffusion through a porous membrane, and the viscosity was measured using an Ostwald viscometer. A comparison of the limiting diffusion currents measured with the calculated currents has shown that Eq. (23a) describes the mass transfer process to not less than one percent accuracy (in this paper the current i_d was measured to about 0.25% accuracy). The simplified expression, Eq. (23), gives a slightly higher value (by about 3% in the most commonly used range of Schmidt number) of the limiting current density.

Another verification method is that of determining the ion diffusion coefficient by means of the RDE method at various concentrations of the indifferent electrolyte and then to extrapolate the value to infinite dilution. The value of D_∞ in infinitely dilute solution so determined can then be compared with the mobility of the ion (λ) calculated from the Einstein relationship: $D_\infty = (RT/F)\lambda$. Since the ion mobility can be determined with great accuracy, the value of diffusion coefficients determined by this method is highly reliable, despite certain indeterminacy caused by extrapolation and the difficulties in the experimental measurement of currents in very dilute solutions (due to the considerable ohmic potential drop). The values of D_∞ obtained by Landsberg *et al.*,⁽³²⁾ for OH^- and H_3O^+ ions, using the expression (23) for the limiting current density, are quite close to the calculated values of the mobilities of these ions, i.e., 5.3×10^{-5} and $9.3 \times 10^{-5} \text{ cm}^2/\text{s}$, respectively (Figure 8).

Summarizing the results of all the investigations devoted to the verification of the theory of mass transfer to a rotating disk, we may conclude that the limiting diffusion current density is quite satisfactorily described to ± 1 percent accuracy by the expression (23a), provided that all the conditions underlying the calculations are satisfied in the experimental work (see the previous section). As already pointed out, the discrepancy between the expressions (23) and (23a) in the range of most frequently used experimental parameters is

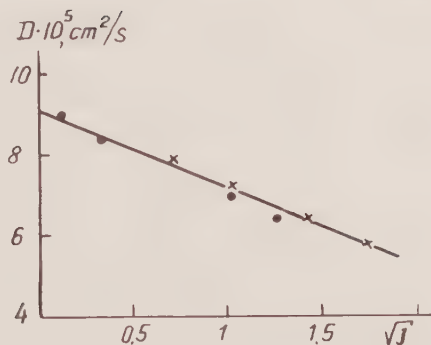


Figure 8. Diffusion of hydrogen ion vs. square root of ionic strength of the solution.⁽³²⁾

not very significant (3 to 5%, which is slightly more than the experimental error). Therefore, a majority of investigators have used Eq. (23) as the most convenient expression in treating experimental results. However, Eq. (23a) should be used in processing the results of precision measurements.

Uniform accessibility of a rotating disk to diffusion has also been demonstrated by special experiments, for example, by measuring the distribution of the thickness of a metal layer deposited on a disk surface by electrocrystallization under limiting diffusion current, as well as by the ring disk electrode method (see below).

5.3. Diffusion Coefficient Measurement

Measurements of the limiting diffusion current and the application of Eq. (23) or (23a) make it possible to determine an important physico-chemical characteristic of a substance reacting on the electrode, i.e., its diffusion coefficient, D . Here it is convenient to make use of the formula:⁽³³⁾

$$D = \eta_{\infty}[(X^{-1} - 0.122939)^{1/2} - 0.1490]^{-3} \quad (33)$$

where $X = i_d / 0.62048nF(\omega\eta_0)^{1/2}c^*$.

The values of D ($\times 10^5$, cm^2/s) determined by the RDE method and by the conventional diffusion technique in a capillary are compared below⁽⁵⁾ for the sake of illustration:

	O ₂	H ₃ O ⁺	Quinone	Hydroquinone
RDE method	1.93	3.83	1.27	0.85
Diffusion in capillary	1.98	3.90	1.30	0.87

In the RDE method of determining D , the concentration c^* and the number of electrons participating in the reaction n are determined in separate experiments. If, however, these values are not known, then instead of the

stationary value of the limiting diffusion current I_d , use is made of the I_d-t curve plotted in the course of prolonged electrolysis through time t of a limited volume of the solution V . Due to gradual diminution in the concentration of the reacting substance, the limiting current drops with time, according to the law:

$$I_d(t) = I_d(0) \exp(-Dt \cdot S/\delta_d V) \quad (34)$$

where $I_d(0)$ is the limiting current at the initial instant of electrolysis and S is the disk surface area. A straight line is plotted in $\ln I_d-t$ coordinates, and the diffusion coefficient D is determined from the slope of this line, using the sequential approximation method.⁽³⁴⁾

If the concentration c^* is known, D and n may be determined separately in one single experiment by measurement of the stationary limiting current in combination with the nonstationary $i-t$ curve plotted with stepwise variation of the electrode potential.⁽³⁵⁾ The following quantities are then determined experimentally from the limiting current [Eq. (23)]:

$$A = i_d \omega^{-1/2} = 0.62 n F \eta_0^{-1/6} D^{2/3} c^* \quad (35)$$

and from the chronoamperometric curve [see below, Eq. (65)]:

$$B = i(t)t^{1/2} = nFD^{1/2}c^* \quad (36)$$

It may be seen that a combination of A/B and $B^{4/3}/A$ makes it possible to determine D and n , respectively.

5.4. Determination of Concentration. Electroanalytical Applications

Since reactant concentration may be determined exactly, the RDE method holds a special place among other electroanalytical techniques. Use of different solid electrode materials makes it possible to utilize a wider range of electrode potentials for electroanalytical purposes than is possible on a dropping mercury electrode. Thus, a wider range of processes may be investigated. The lower detection limit for the analytical determination is estimated (for reversible electrode reactions⁽²⁹⁾) to be 10^{-7} mole/L. The RDE method, even its simplest version, is superior for such measurements to "classical" (d.c.) polarography, mainly due to low charging current (as a result of the constant area of the electrode surface during analysis).

In order to increase the accuracy and sensitivity of measurement, programmed modulation of the electrode rotation speed (the so-called hydrodynamic voltammetry) has been suggested.⁽³⁶⁾

This nonstationary method will be considered in greater detail in Section 7.5. Here we note that, unlike the potential modulation technique extensively

used in electroanalysis, no interfering non-Faradaic (i.e., capacitive) current (caused by the changes in electrode charge) is generated in the rotation speed modulation experiments. Therefore, the detection limit in the hydrodynamic voltammetry analysis may be as low as 5×10^{-8} mole/L⁽³⁶⁾; consequently, it is one of the most sensitive voltammetric techniques.

A stationary method of separating reactions that run in parallel on the rotating disk electrode has been described.⁽³⁷⁾ If one reaction is diffusion limited, while the other is not, the total current through the cell may be expressed as:

$$I = I_d + I_k = a\omega^{1/2} + b \quad (37)$$

where a and b are constants which do not depend on the electrode rotation speed. On extrapolating the current to $\omega \rightarrow 0$, both the components of the total current can be readily separated. Figure 9 shows a graphical method for resolution of two processes by this technique.

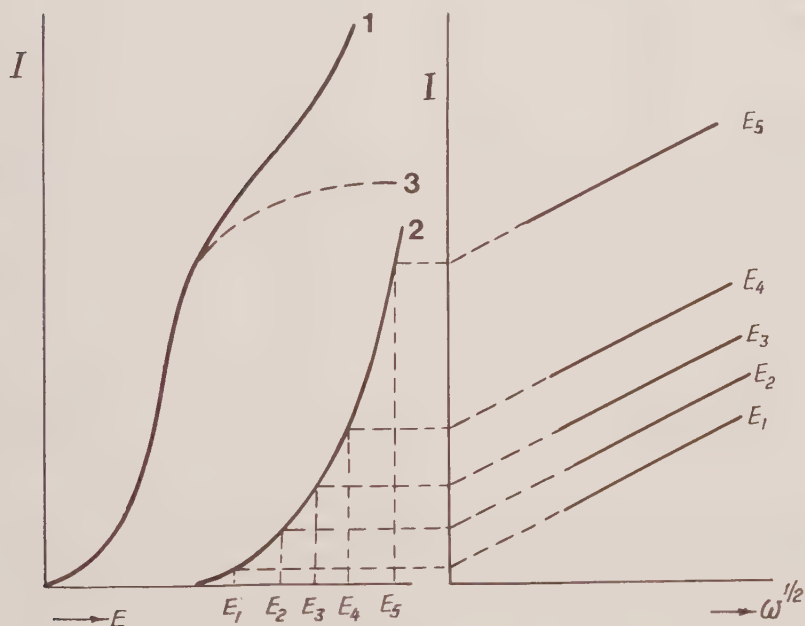


Figure 9. A scheme for graphical separation of two processes occurring simultaneously on an RDE. Left: experimental I - E curve (1) separated into two curves: for diffusion limited (3) and diffusion non-limited (2) currents. Right: dependences of the measured current (from curve 1, left) on $\omega^{1/2}$ for different potentials. I values obtained by extrapolation to $\omega \rightarrow 0$ are further used to construct curve 2 (left); subtracting curve 2 from curve 1 gives curve 3.

6. Principles of Investigations of Kinetics of Electrochemical Reactions

6.1. Basic Relationships

The formulas derived in Section 3 for the limiting diffusion current at an RDE provide an opportunity to analyze the influence exerted by the transport of reagents to the electrode surface on the total rate of the electrochemical process. In this way, it is possible to establish the type of kinetic equation describing the rate of the electrochemical step.

Consider a simple first-order redox reaction:



where *Ox* is the oxidized form and *Red* is the reduced form of the reacting substance. The formal rate constants, k_f and k_b , of the corresponding reactions depend on the electrode potential.

The dependence of the current i on the overpotential η applied can be expressed in the following form [see, for instance, Reference (38)]:

$$i = i_0 \{ (c_{OS}/c_O^*) \exp(-\alpha n F \eta / RT) - (c_{RS}/c_R^*) \exp[(1 - \alpha) n F \eta / RT] \} \quad (39)$$

where i_0 is the exchange current density, and c_O^* and c_R^* are the concentrations of the corresponding forms in the solution bulk, and α is the transfer coefficient.

For the μ -order redox reaction, we have:



and the dependence of the current density on the overpotential may be written as:

$$i = i_0 \{ (c_{OS}/c_O^*)^\mu \exp(-\alpha n F \eta / RT) - (c_{RS}/c_R^*) \exp[(1 - \alpha) n F \eta / RT] \} \quad (40)$$

For more complex electrochemical processes, the kinetic equations are of more intricate form. In general, one of the two partial currents may be neglected sufficiently far away from the equilibrium potential ($n F \eta / RT \gg 1$); thus, only one exponential term will remain in Eq. (39).

The aim of electrochemical investigation lies in determining the parameters i_0 , μ , and α . This may be carried out in a comparatively simple manner, provided that no diffusion complications arise. In practice, it is not always possible to entirely eliminate the influence of the mass transfer process. As shown below, this may be achieved using the RDE method.

At a given polarization of the electrode ($\eta = \text{const.}$), let the kinetic equation describing the reduction reaction be:

$$i = i_0 \exp(-\alpha n F \eta / RT) (c_{OS} / c_O^*)^\mu \quad (41)$$

Let:

$$i_k = i_0 \exp(-\alpha n F \eta / RT) \quad (42)$$

denote the density of "true" kinetic current, i.e., the current not distorted by the deviations of Ox concentration near the electrode from that in the solution bulk. From Eq. (19), using Eq. (22):

$$c_{OS} / c_O^* = 1 - i / i_{dO} \quad (43)$$

substituting Eqs. (42) and (43) into Eq. (41), we obtain the following equation:

$$i / i_k = (1 - i / i_{dO})^\mu \quad (44)$$

where i_{dO} is the density of the limiting diffusion current of the oxidized form.

Equation (44) is equivalent to Eq. (41) and relates the density of the measured current i to the parameters i_k and μ of the electrochemical reaction. Graphic methods are generally applied to solve Eq. (44).

Now we shall pass on to practical methods for determining i_k and μ . For this purpose, we shall turn our attention to the dependence of the measured current on the electrode rotation speed at constant η .

The general pattern of i vs. $\omega^{1/2}$ dependence over a wide rotation speed range is shown in Figure 10. The physical interpretation of this curve is as follows: at low electrode rotation speeds, where $i_{dO} \ll i_k$, diffusion constraints are decisive and the measured current coincides with the limiting diffusion current, i.e., $i \approx i_{dO}$. According to Eq. (23), i_{dO} is proportional to $\omega^{1/2}$; moreover, $c_s \rightarrow 0$ (diffusion control). At higher rotation speeds constraints

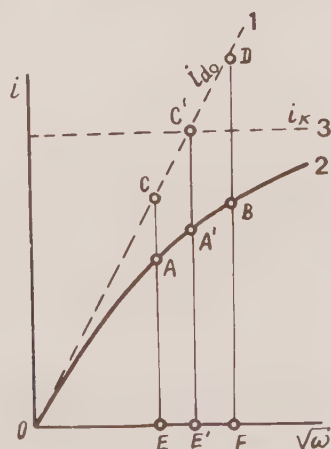


Figure 10. A scheme for the determination of the reaction order: dependence of the measured current (2) the calculated diffusion current i_{dO} (1), and the kinetic current i_k (3) on $\omega^{1/2}$.

associated with the finite rate of electrochemical transformation on the electrode surface ($i_{dO} \gg i_k$) play a decisive role. The current at the electrode approximates to i_k ($i \approx i_k$) and in the limit does not depend on the rotation speed, and $c_s \approx c^*$ (kinetic control). Mixed control holds valid where there are comparable values ($i_k \approx i_{dO}$).

On the $i-\omega^{1/2}$ curve shown in Figure 10 (curve 2), let us choose two currents $i^{(1)}$ and $i^{(2)}$ (points A and B), corresponding to two different values of angular velocity, ω_1 and ω_2 (points E and F). According to Eq. (44), for the two rotation speeds, we may write:

$$i^{(1)}/i_k = (1 - i^{(1)}/i_{dO})^\mu \quad (45a)$$

$$i^{(2)}/i_k = (1 - i^{(2)}/i_{dO})^\mu \quad (45b)$$

Taking the logarithm of the ratio of Eq. (45a) to Eq. (45b), we obtain the following expression for μ from the two experimental values of the current:

$$\mu \ln \frac{1 - i^{(1)}/i_{dO}}{1 - i^{(2)}/i_{dO}} = \ln \frac{i^{(1)}}{i^{(2)}} \quad (46)$$

For each rotation speed, the value of i_{dO} is calculated using Eq. (20).

Then the following formula may be used to determine μ :

$$\mu = \frac{\ln BF - \ln AE}{(\ln CE - \ln AC) - (\ln DF - \ln BD)} \quad (47)$$

which, as can easily be verified, is equivalent to Eq. (46). By substituting the length of the corresponding intervals in Eq. (47), we obtain the value of μ .

In practice, however, certain shortcut techniques may be used for calculating μ . These techniques consist in choosing the points A and B in a special manner.⁽³⁹⁾ Thus, for instance, if B is taken essentially in the kinetic region (which may be effected by increasing the rotation speed, ω , or by extrapolating the experimental data to the region, $\omega \rightarrow \infty$), the interval BF becomes equal to i_k , and $BD \approx DF$. Equation (47) then takes the form:

$$\mu = \frac{\ln i_k - \ln i}{\ln i_{dO} - \ln (i_{dO} - i)} \quad (48)$$

where i is the value of the current at a certain rotation speed ω (point A), and i_{dO} is the value of the limiting diffusion current at the same rotation speed. The magnitude of i_k is determined on passing to the limit $\omega \rightarrow \infty$. This requires a judicious choice of η .

To determine i_k from the experimental data, we shall assume that the reaction order μ is known. Thus, according to Eq. (44), we have:

$$i_k = i(1 - i/i_{dO})^{-\mu} \quad (49)$$

Substituting the experimental value of i and the value of i_{dO} calculated by Eq. (20) for the same rotation speed, we can then obtain the value of i_k .

Theoretical considerations are significantly simplified if the electrochemical reaction is first order. For $\mu = 1$, Eq. (49) may be solved directly:

$$i = i_k i_{dO} / (i_k + i_{dO}) \quad (50)$$

We can rewrite this equation in a slightly different form, which is commonly used in practice:

$$1/i = 1/i_k + 1/i_{dO} \quad (51)$$

This formula may be interpreted in the following terms: in the case of mixed kinetics, the total "resistance" limiting the electrode process rate is made up of the resistance due to reagent transport and the resistance of the electrochemical reaction proper.

Since $i_{dO} \propto \omega^{1/2}$, Eq. (51) is represented by a straight line on a $1/i - 1/\omega^{1/2}$ plot (Figure 11). The intercept on the ordinate when this line is extrapolated to large rotation speeds is equal to $1/i_k$. This gives an easy means of calculating the density of the "true" kinetic current, i_k .

Now we shall take up the general kinetic equation Eq. (40) for the redox reaction of the first order. We change the variable according to Eq. (43), thus:

$$c_{OS}/c_O^* = 1 - i/i_{dO}; \quad c_{RS}/c_R^* = 1 + i/i_{dR} \quad (52)$$

where i_{dO} and i_{dR} are the densities of the limiting diffusion currents of *Ox* and *Red* forms, respectively. The unlike signs in Eq. (52) show that the fluxes of the *Ox* and *Red* forms are in opposite directions.

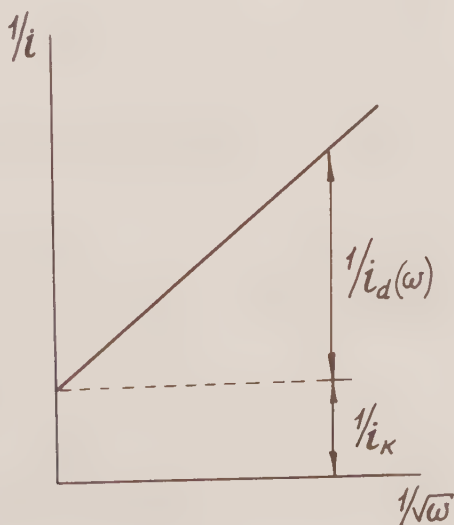


Figure 11. A scheme for the determination of kinetic current (case of mixed kinetics).

Substituting Eq. (52) into Eq. (40), and after simple transformation, we obtain:

$$1/i = b^\alpha/[i_0(1-b)] + \{[1/(D_O^{2/3}c_O^*)] + [b/(D_R^{2/3}c_R^*)]\}1.61\eta_0^{1/6}/(1-b)nF\omega^{1/2} \quad (53)$$

where

$$b = b(\eta) = \exp(nF\eta/RT).$$

According to Eq. (53), the plot of $1/i$ against $1/\omega^{1/2}$ is again a straight line. This line can be constructed from the experimental data obtained for different ω , at a constant overpotential η . The intercept of this line of the ordinate axis corresponds to the first term on the right-hand side of Eq. (53) and may be used in determining the true kinetic current, i_k :

$$i_k = i_0(1-b)b^{-\alpha} = i_0\{\exp(-\alpha nF\eta/RT) - \exp[(1-\alpha)nF\eta/RT]\} \quad (54)$$

The results given above refer to a comparatively simple power dependence of the electrochemical reaction rate on the reagent concentration [Eq. (40)]. If this dependence is of more generalized type:

$$i = nFk(\eta)f(c_{OS}) \quad (55)$$

then it is much more difficult to establish the form of the function $f(c_{OS})$ and to determine the kinetic current:

$$i_k = nFk(\eta)f(c_O^*) \quad (56)$$

As an example, we will consider an electrode reaction which is preceded by the adsorption stage. In this case, $f(c_{OS})$ is described by an adsorption isotherm equation of some given type.

Due to the constraints imposed by the mass transfer stage, the kinetic equation (55) takes the form:

$$i = i_k f(c_O^*(1 - i/i_{dO}))/f(c_O^*) \quad (57)$$

Considering a particular case, where charge transfer is preceded by equilibrium adsorption of reacting particles, the function $f(c_{OS})$ may be represented by:

$$f(c_{OS}) = ac_{OS}^{1/x}/(1 + ac_{OS}^{1/x}) \quad (58)$$

where a is the adsorption coefficient, and x is the number of the reacting particles formed during chemisorption of the initial particles. Equation (58) corresponds to the Langmuir adsorption isotherm.

The kinetic equation (58) then takes the following form:

$$1/i = 1/i_k \{ ac_O^{*1/x} / (1 + ac_O^{*1/x}) + 1 / [(1 + ac_O^{*1/x})(1 - i/i_{dO})^{1/x}] \} \quad (59)$$

This parameters a and x in the adsorption equation (59) can be found from a direct analysis of Eq. (59) expressed in $1/i - 1/(1 - i/i_{dO})$ coordinates.⁽⁴⁰⁾

6.2. Measurement of Kinetic Characteristics of Electrode Reactions

Measurement of kinetic parameters such as rate constant, transfer coefficient, or exchange current, does not involve serious difficulties if the reaction takes place in the kinetic regime, i.e., mass transfer is rapid and the electrochemical stage itself is rate determining. If, however, the rates of these two consecutive stages are comparable (mixed kinetics) then, as expected from the above, concentration polarization has a significant influence on the potential dependence of the current. The use of the RDE makes it possible to "eliminate the diffusion limitations" and to obtain the current-voltage curve without distortion by the concentration polarization. This results from the specific mass transfer rate versus rotation speed dependence inherent in the RDE. As demonstrated in Section 6.1, the problem is considerably simplified if the electrode reaction is first order with respect to the reactant concentration. We shall confine ourselves to this case [for discussion of n th order reactions see Reference (40)].

The mixed kinetic regime can be recognized by the shape of the experimental current versus square root of the rotation speed curve. This dependence is less pronounced than the dependence for the limiting diffusion current (cf., Figures 10 and 12). Indeed, as the speed ω changes, not only does the thickness of the diffusion layer δ_d vary, but the near-electrode concentration c_s also changes simultaneously. This change partially compensates for the effect of speed on δ_d in the diffusion current.

The $1/i - 1/\omega^{1/2}$ curve is plotted in order to elicit the kinetic and diffusion currents from the measured current. In fact, from Eqs. (51) and (23), it follows that:

$$\frac{1}{i} = \frac{1}{nFkc^*} + \frac{1.61\eta_0^{1/6}}{nFD^{2/3}c^*} \cdot \frac{1}{\omega^{1/2}} \quad (51a)$$

It is seen that the slope of this line characterizes mass transport and may be used to determine D , c^* and n . The intercept of this line on the ordinate gives the kinetic current. "Elimination of the diffusion limitations" thus reduces to graphic extrapolation of the current to an infinitely great rotation speed at which the near-electrode concentration of the reacting substance may be taken to be equal to its concentration in the bulk solution. After conducting such an analysis for different overpotentials, we obtain the "true" polarization curve

from which the exchange current, transfer coefficient, etc., may be found in the usual way. Kinetic parameters for various reactions obtained using the RDE method are listed in References (10) and (11).

To illustrate the use of this method, the i against $\omega^{1/2}$ and $1/i$ against $1/\omega^{1/2}$ curves relating to the ionization of chlorine on platinum at moderate overpotential⁽³⁹⁾ are shown in Figures 12 and 13. Here we may neglect the reverse reaction and make use of Eq. (51a). The reaction order was determined to be close to unity, which follows from the straight $1/i-1/\omega^{1/2}$ relationship shown in Figure 13.

For very fast reactions the mixed regime only exists in close proximity to the equilibrium potential. Consequently, the reverse reaction should be taken into consideration in the analysis [see Eq. (53)]. Jahn and Vielstich⁽⁴¹⁾ used the RDE method to measure the rate constant in the rapid redox system $\text{Fe}^{2+}/\text{Fe}^{3+}$ (Figure 14). The value thus obtained was close to the rate measured by conventional AC techniques. The RDE method, nevertheless, has certain advantages over the AC technique (and other relaxation methods), since it is not necessary to correct for or to eliminate the influence of the electrical double layer capacity. According to the estimates reported in Reference (41), rate constants up to 0.1 cm/s may be measured using the RDE method.

The method described above for "elimination of diffusion limitations" by extrapolating to $\omega \rightarrow \infty$ is rather laborious, since a series of current measurements at various rotation speeds and at each potential value are required, with graphic analysis. An alternative procedure is that of studying kinetics by plotting the polarization curves "at a given near-electrode concentration of the reacting substance."⁽⁴²⁾ It is based on the fact that $i/\omega^{1/2}$ completely determines the value of the near-electrode concentration c_s [see formula (20)]. Therefore, it suffices to maintain the ratio $i/\omega^{1/2}$ constant in plotting the polarization curve (by using an appropriate programming device which monitors the electrode drive motor speed) to avoid the indeterminacy in c_s . Unlike the value obtained by extrapolating to $\omega \rightarrow \infty$, the current measured by this method is not the "true" kinetic current in the sense defined above, because it is related to some lesser (but exactly known) concentration rather than to the bulk concentration c^* of the electroactive substance.

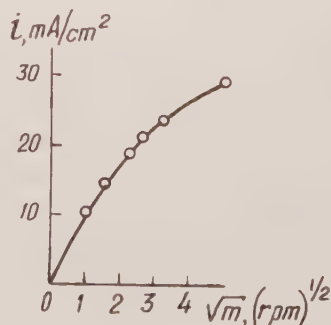


Figure 12. Limiting current density of chlorine ionization on Pt electrode vs. square root of the angular velocity.⁽³⁹⁾ Solution: 0.1 HClN + 1.9 N H_2SO_4 ; overpotential: 0.04 V.

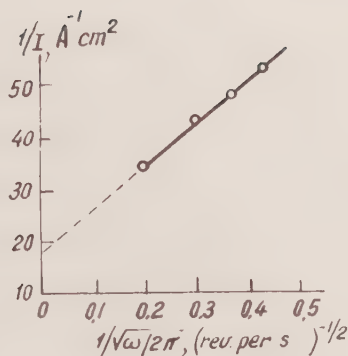


Figure 13. Plot of $1/i$ vs. $1/(\omega/2\pi)^{1/2}$ as per Figure 12.

7. Nonstationary Processes

7.1. Qualitative Considerations

Nonstationarity arising at RDE may be due either to the nonstationary hydrodynamic conditions or to time-varying conditions at the electrode surface. In both cases, the rate of convective mass transfer to the disk surface undergoes changes which are measured as a time variation in the current flowing through the cell.

Theoretical estimates that have been substantiated by experimental observations suggest that the time to establish stationary conditions of electrode reaction rate in systems with forced convection is considerably less than that

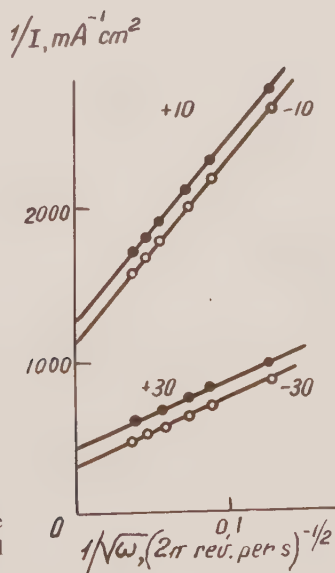


Figure 14. Determination of the reaction rate constant in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ system⁽⁴¹⁾: plot of $1/i$ vs. $1/\omega^{1/2}$ (overpotential in mV is shown on curves).

in cells with natural convection. Therefore, the transition characteristics of electrochemical systems can be conveniently studied with the help of the RDE. These characteristics usually carry more information about the process under investigation than do stationary measurements. Thus, for example, in addition to the information about the number of electrons transferred, which can be derived from measurements of the stationary diffusion current at an RDE, we can obtain information about the rates of electrode processes, adsorption, etc., from the nonstationary measurements.

First, we will consider the establishment of a stationary regime when (a) the disk rotation speed is changed and (b) when electrode polarization is changed.

In the first case, the rate of establishing a stationary regime wholly determined by the action of viscous stresses generated in the liquid. Thus, when a disk at rest is suddenly set in motion at an angular velocity of ω , a liquid layer of thickness $\delta_0 \sim \sqrt{\eta_0/\omega}$ is forced into rotational motion. The time τ_0 needed to establish stationary flow (see Section 2) is about $\tau_0 \sim \delta_0^2/\eta_0$ or $\tau_0 \sim 1/\omega$.

Unlike the hydrodynamic phenomena, relaxation of convective diffusion takes place at distances of the order of the diffusion boundary layer thickness, δ_d . Concentration is equalized by the diffusion mechanism: the relaxation time of the diffusion process is $\tau_d \sim \delta_d^2/D$.

By comparing τ_0 and τ_d , it is easy to show that:

$$\tau_0/\tau_d \sim (D/\eta_0)^{1/3} = Sc^{-1/3}$$

At high Sc (for usual aqueous solutions $Sc \sim 10^3$), the transfer of momentum in a medium proceeds at a much faster rate than that of matter and the relaxation of hydrodynamic perturbations takes place much faster than the relaxation of the diffusion processes ($\tau_0 \ll \tau_d$). It is therefore easy in practice to modulate electrode rotation speed in such a manner that diffusion always remains a quasi-stationary process (this principle underlies a new electrochemical method—hydrodynamic voltammetry; see Section 5.4.).

In the following pages we will consider the relaxation of the diffusion process, since this type of nonstationary phenomena is common in electrochemistry.

7.2. Establishment of Limiting Diffusion Current

If the surface of an RDE exhibits uniform electrochemical activity, nonstationary processes take place uniformly over the electrode. The variation in the reagent concentration near the disk is described by the equation of nonstationary convective diffusion:

$$\frac{\partial c}{\partial t} + v_z \frac{\partial c}{\partial z} = D \frac{\partial^2 c}{\partial z^2} \quad (60)$$

where t is the time variable. As already mentioned in Section 3, for diffusion in, e.g., aqueous solution, $Sc = \eta_0/D \gg 1$, and we can express v_z using Eq. (16a).

Since the process of establishing the stationary condition of convective diffusion is located within the layer δ_d , it is convenient to use the dimensionless variables:

$$\xi = z/\delta_d \quad \text{and} \quad \tau = Dt/\delta_d^2 \quad (61)$$

Equation (60) then takes the form:

$$\frac{\partial c}{\partial \tau} + \left(\frac{v_z \delta_d}{D} \right) \frac{\partial c}{\partial \xi} = \frac{\partial^2 c}{\partial \xi^2} \quad (61a)$$

On substituting the expressions for v_z and δ_d from (16a) and (18) into (60a), we obtain:

$$\frac{\partial c}{\partial \tau} - a \xi^2 \frac{\partial c}{\partial \xi} = \frac{\partial^2 c}{\partial \xi^2} \quad (62)$$

where the numerical factor $a = 2.13$.

The basis of the problem of establishing the stationary limiting diffusion current may be considered to be an instantaneous change of electrode potential via an external source. For instance, consider a transient from the equilibrium value to η . If the magnitude of this transient is sufficiently great, the current will be determined by the rate of transport of the electroactive solution component to the electrode surface. The reagent concentration near the surface depends on the electrode potential, and the variation in the current depends on the rate of concentration variation near the electrode.

Equation (62) should, therefore, be supplemented with the following boundary conditions:

$$c = c^* \quad \text{for } \tau = 0, \xi \geq 0; \quad (63a)$$

$$c = c_s \quad \text{for } \tau > 0, \xi = 0; \quad (63b)$$

$$c \rightarrow c^* \quad \text{for } \tau > 0, \xi \rightarrow \infty \quad (63c)$$

where c_s is the concentration in the vicinity of the electrode surface corresponding to the new potential value.

The problem of establishment of stationary diffusion current has been solved by various methods. Here we shall cite the result obtained in Reference (43) with the help of a special approximation method [for details, see Reference (7)].

If discharge of a reagent is accompanied by transfer of n electrons, then the following relationship has been obtained in Reference (43) for the diffusion

current at the RDE:

$$i(t) = (nFD(c^* - c_s)/\delta_d) \times \{[\exp(-3.10Dt/\delta_d^2)/(\pi Dt/\delta_d^2)^{1/2}] + 0.94 \operatorname{erf}(3.10Dt/\delta_d^2)^{1/2}\} \quad (64)$$

where $\operatorname{erf}(u) = (2/\pi^{1/2}) \int_0^u \exp(-z^2) dz$ is the probability integral.⁽²¹⁾ Using Eq. (64), it is easy to analyze the establishment of the stationary regime for convective diffusion.

In the initial instants of time ($t \ll \delta_d^2/3.10D$), the current to the electrode is purely of a diffusion type, convection having hardly any effect on the current:

$$i = nFD(c^* - c_s)/(\pi Dt)^{1/2} \quad (65)$$

As the diffusion front recedes from the electrode, the convective mechanism of transfer becomes predominant. The stationary regime begins to set in when the diffusion front is away from the electrode surface at a distance δ_d , i.e., reaches the boundary of the diffusion boundary layer formed near the electrode under stationary conditions. If $t \gg \delta_d^2/3.10D$, expression (64) can be simplified to:

$$i = 0.94nFD(c^* - c_s)/\delta_d \quad (66)$$

i.e., the current density nearly coincides with the value obtained earlier [Eq. (20)] for stationary regime to about 6 percent accuracy. The discrepancy between Eq. (66) and Eq. (20) is due to the approximation method used in Reference (43) to solve the non-stationary problem.

The calculation results are illustrated in Figure 15, which shows the time variation of the current for reduction of Cu^{2+} on a rotating gold electrode

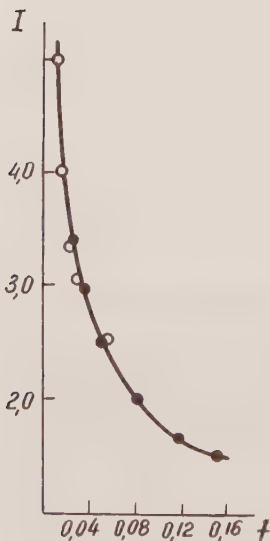


Figure 15. Time dependence of current (in dimensionless units) under stepwise change of RDE potential from stationary value to the limiting current potential.⁽⁴⁴⁾ Reduction of Cu^{2+} (O, $1.9 \times 10^{-3} M$; ●, $3.91 \times 10^{-3} M$) in 0.5 M KCl solution on gold electrode.

when its potential is changed stepwise from the stationary value to a value in the region of the limiting current. The solid line⁽⁴⁴⁾ shows the current variations according to Eq. (64).

Despite the error in the magnitude of the stationary current given by Eq. (66), the approximate method developed in Reference 43 is quite useful in studying a wide range of non-stationary processes occurring on an RDE.

7.3. Polarization of Electrode with a Linear Potential Sweep

Polarization of an electrode by a potential which varies in time according to a linear law is widely used in electroanalytical (linear and cyclic voltammetry), kinetic (potentiodynamic curves) and other studies. The computation method described above provides a means of theoretically studying the non-stationary processes occurring in this case.

Consider the redox reaction of Eq. (38) under conditions where the rate of the electrode process is limited by the stages of transport of components to the disk surface.

The convective diffusion equations for both components are:

$$\begin{aligned}\frac{\partial c_O}{\partial t} + v_z \frac{\partial c_O}{\partial z} &= D \frac{\partial^2 c_O}{\partial z^2} \\ \frac{\partial c_R}{\partial t} + v_z \frac{\partial c_R}{\partial z} &= D \frac{\partial^2 c_R}{\partial z^2}\end{aligned}\tag{67}$$

where c_O and c_R are the concentrations of the oxidized and reduced forms, respectively. These equations must be supplemented with the following boundary conditions:

$$D \left(\frac{\partial c_O}{\partial z} \right)_s = -D \left(\frac{\partial c_R}{\partial z} \right)_s \tag{68a}$$

$$(c_{Os}/c_O^*) = (c_{Rs}/c_R^*) \exp(nF\eta/RT) \tag{68b}$$

where c^* and c_s are the concentrations of the corresponding substances in the solution bulk and near the electrode surface, and η is the overpotential. For the sake of simplicity, the diffusion coefficients of both the components have been taken to be equal.

The first boundary condition [Eq. (68a)] implies conservation of matter during electrochemical transformation, while the second [Eq. (68b)] means that the kinetics of the electrode reaction retains its quasi-equilibrium nature when the polarizing potential is applied.

We shall assume that the polarizing potential changes according to the linear law:

$$\eta = gt = \sigma_0 \tau$$

where g is the polarization potential sweep rate, and:

$$\sigma_0 = nFg\delta_d^2/RTD \quad \text{and} \quad \tau = Dt/\delta_d^2$$

The approximate method of analyzing non-stationary convective diffusion⁽⁷⁾ resulted in the following current dependence at the RDE on τ :

$$i = i_{dO}\sigma_0[(1 + c_R^*/c_O^*)/4] \int_0^\tau [\exp(-3.10\lambda)/(\pi\lambda)]^{1/2} + 0.94 \operatorname{erf}(3.10\lambda)^{1/2} \{\cosh^2[\sigma_0(\tau - \lambda - \tau_{1/2})/2]\}^{-1} d\lambda \quad (69)$$

where $\tau_{1/2} = \ln(c_O^*/c_R^*)/\sigma_0$. As before, i_{dO} is the limiting diffusion current of the oxidized form (for the sake of example, only the cathode polarization is considered here).

We shall now examine certain specific features of relationship (69). A direct analysis of Eq. (69) shows that, after a sufficiently large time has elapsed ($t \gg \delta_d^2/D$), the current at the electrode is equal to the limiting diffusion current of the oxidized form, i.e.:

$$i \rightarrow i_{dO}$$

The pattern of the time variation of i essentially depends on the parameter σ_0 , i.e., on the ratio between the potential sweep rate and the electrode rotation rate.

At fast potential sweeping ($\sigma_0 \gg 1$), a maximum appears on the $i(\tau)$ curve, which means that $i(\eta)$ has a maximum. The position and magnitude of this maximum are practically the same as those of maxima on similar curves plotted for systems without forced convection.

On the contrary, if $\sigma_0 \ll 1$, i.e., potential variation takes place very slowly, diffusion processes are able to keep in step with the variation in the polarizing potential. The diffusion process may be regarded as quasi-stationary and the time variation of the current is described by the following relationship:

$$i = i_{dO}(1 - \exp \eta)/(1 + c_O^* \exp \eta/c_R^*) \quad (71)$$

The transition from a nonstationary to quasi-stationary diffusion pattern is seen in Figure 16, which shows typical current-voltage curves plotted for the reduction of thallium ion on amalgamated copper electrode.⁽⁴⁵⁾

7.4. Electrochemical Impedance

If a periodically varying potential, $\tilde{\eta}(t)$, is superimposed on the main overpotential, $\bar{\eta}$, which polarizes the cell, then

$$\eta = \bar{\eta} + \tilde{\eta}(t) \quad (72)$$

A variable component appears in the Faradaic current flowing through the cell. It may be expected that the Faradaic current $\hat{i}(t)$ generated under

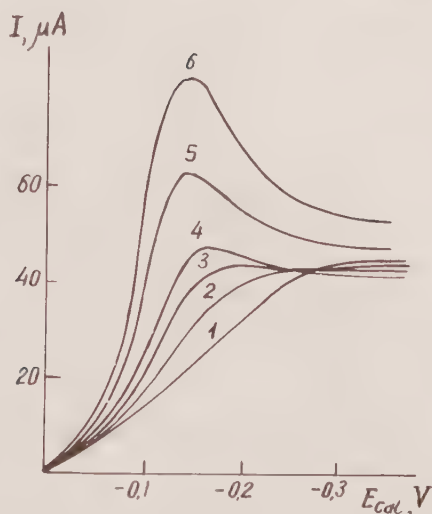


Figure 16. Polarogram of Tl^+ reduction in $5 \times 10^{-2} \text{ N LiClO}_4$ on amalgamated copper electrode.⁽⁴⁵⁾ Rotation speed 2300 rpm, potential sweep rate (V/s): (1) 0.0125; (2) 0.1; (3) 0.4; (4) 1.6; (5) 4.0; (6) 8.0.

the action of the harmonic signal $\tilde{\eta}(t)$ of low amplitude is superimposed on the main Faradaic current:

$$i = \bar{i} + \tilde{i}(t) \quad (73)$$

The magnitude of $\tilde{i}(t)$, being dependent on the amplitude of the harmonic component of the overpotential $\tilde{\eta}(t)$, clearly also depends on the frequency f of the harmonic signal, and on the nature of the Faradaic process at the electrode. The relationship between $\tilde{i}(t)$ and $\tilde{\eta}(t)$, which for a low signal is probably a linear function:

$$i(t) = \mathcal{Z}\tilde{\eta}(t) \quad (74)$$

is the requirement for calculating electrochemical impedance. An investigation into the dependence of impedance $\mathcal{Z}$ on the frequency f of the applied harmonic signal yields information on the kinetics of the reactions taking place at the electrode.

When periodic changes in the electrode potential occur, the concentration of the solution components participating in the electrochemical reaction also changes. Concentration changes occur in the bulk solution to distances of the order of $\delta_f = (D/f)^{1/2}$ where D is the molecular diffusion coefficient.

Let us isolate as usual the real and the imaginary parts of impedance, designating them as resistance R_s and pseudo-capacitance C_s , respectively:

$$\text{Re}(\mathcal{Z}) = R_s \quad \text{and} \quad \text{Im}(\mathcal{Z}) = -1/fC_s$$

At high frequencies, $f \gg D/\delta_d^2$, when the outer boundary of the variable concentration layer is not too distant from the electrode surface ($\delta_d \gg \delta_f$), convective motion of solution has little effect on periodic concentration changes. Under diffusion control, the value of the impedance of the rotating

disk electrode does not depend on rotation rate ω and coincides with the usual Warburg diffusion impedance:

$$R_s = \frac{1}{fC_s} = \left(\frac{1}{c_R^*} + \frac{1}{c_O^*} \right) \frac{RT}{(nF)^2} \frac{1}{(2fD)^{1/2}} \quad (75)$$

On the contrary, at low frequencies, when $f \ll D/\delta_d^2$ or $\delta_d \leq \delta_f$, the concentration changes occur in the solution region in which convective motion already exerts significant influence. This leads to additional resistance in transport of reagents. At the limit $f \rightarrow 0$, impedance is pure resistance:

$$R_s \rightarrow \left(\frac{1}{c_R^*} + \frac{1}{c_O^*} \right) \frac{RT}{(nF)^2} \frac{\delta_d}{D}; \frac{1}{fC_s} \rightarrow 0 \quad (76)$$

For calculation of the impedance $\mathcal{Z}$ at intermediate frequencies, see References (7) and (46).

7.5. Electromechanical Impedance

Application of programmed modulation of the rotation speed of the disk electrode by means of a special device holds promise for investigation of electrode processes, particularly those which involve reactions proceeding under diffusion control (see above, pp. 312 and 322). The rotation rate changes disturbing the pattern of solution motion in the vicinity of the disk ultimately lead to a change in the magnitude of electrode current. Evidently, these changes are most marked when the limiting diffusion current is recorded. The fluctuations have a very slight effect on the rate both of the electrochemical step proper and on that of the reduction or formation of surface films, etc. The capacitive component of current is also little affected, which unlike the generally used methods of electrode potential modulation, allows much greater precision in measuring the Faradaic current of the reaction. Initially,⁽³⁶⁾ the rotation rate of the disk electrode was modulated according to the sine law:

$$\omega^{1/2} = \omega_0^{1/2}(1 + \varepsilon \cos \Omega t)$$

The frequency Ω and depth $\varepsilon = \Delta\omega^{1/2}/\omega_0^{1/2}$ of modulation were varied in a sufficiently wide range.

To the first harmonic approximation the corresponding disk current modulation can be represented as:

$$i = i_{\omega_0} + \Delta i_1 \cos(\Omega t - \phi_1)$$

The values of Δi_1 and ϕ_1 associated with certain electrode process characteristics are measured by a phase-sensitive amplifier. This makes it possible to employ hydrodynamic voltammetry both for electroanalysis (see above, Section 5.4) and for investigation of the kinetics and mechanism of electrode processes.⁽⁴⁷⁾

At a low depth of modulation of electrode rotation rate,

$$\omega = \omega_0 + \tilde{\omega}(t)$$

where $\tilde{\omega}(t)$ is the periodic variation of rotation rate ($\tilde{\omega} \ll \omega_0$), by analogy with electrochemical impedance $\mathcal{Z}$ [see Eq. (74)], it is possible to introduce electromechanical impedance $\mathcal{Z}_m$, which is determined by means of the relation:

$$\Delta \tilde{i} = \mathcal{Z}_m \tilde{\omega}$$

By measuring the active and the reactive components of impedance $\mathcal{Z}_m$ it is possible in principle to separate the diffusion-limited and the kinetics-limited components of the total current through the electrode, i.e., to solve the same problem for which the steady state method described in Section 5.4 was developed, but with a very small change of electrode rotation rate.⁽⁴⁸⁾

8. Investigations of the Kinetics of Homogeneous Chemical Reactions

The RDE technique is extensively used in studying electrode processes which are complicated by chemical reactions of electrochemically active substances on the electrode surface and in the near-electrode layer. Depending on the sequence in which the chemical stage and charge transfer stage occur, we can distinguish the following typical cases: (1) the chemical reaction precedes the electrochemical stage, (2) chemical and electrochemical stages take place in parallel, and (3) the chemical reaction proceeds after the electrochemical reaction. The case where the chemical stage occurs "between" two electrochemical stages (the so-called ECE mechanism) is more complicated.

A general method of analyzing the so-called kinetic and catalytic current at an RDE is described in Reference 7.

8.1. Preceding Chemical Reaction

Let the electroreduction stage of a substance A_1 be preceded by the stage of its chemical formation from the substance A_2 , which is inactive in the potential range investigated. Let us represent the whole process by the following scheme:



where ρ and $\rho\sigma$ are the rate constants of the corresponding chemical reactions;

$$\sigma = c_2/c_1 \quad (79)$$

is the chemical equilibrium constant, and c_1 and c_2 are the concentrations of A_1 and A_2 , respectively.

If the chemical equilibrium is shifted toward the formation of the electroactive substance A_1 , i.e., $c_1 \gg c_2$ and $\sigma \ll 1$, then the chemical conversions have little effect on the density of the current due to the reduction of A_1 . When the reduction reaction is very fast, the current density is almost the same as the limiting diffusion current density i_{d_1} for the substance A_1 .

If, on the contrary, chemical equilibrium is shifted toward the formation of the inactive substance A_2 , the current flowing in the cell is wholly determined by the rate of the chemical stage, Eq. (77).

The equations of the convective diffusion for A_1 and A_2 in the vicinity of a rotating disk electrode now take the form:

$$v_z \frac{dc_1}{dz} = D \frac{d^2 c_1}{dz^2} + \rho(c_2 - \sigma c_1) \quad (80a)$$

$$v_z \frac{dc_2}{dz} = D \frac{d^2 c_2}{dz^2} - \rho(c_2 - \sigma c_1) \quad (80b)$$

The additional terms on the right-hand side of Eqs. (80a) and (80b) are associated with the mutual reactions of the substances transported in the solution.

At distances remote from the electrode surface, the concentrations assume "bulk" values:

$$c_1 \rightarrow c_1^*, c_2 \rightarrow c_2^*; c_2^*/c_1^* = \sigma \quad \text{as } z \rightarrow \infty \quad (81)$$

In the potential range under consideration, the substance A_2 is inactive, while A_1 undergoes instantaneous reduction on the electrode:

$$D(dc_2/dz)_s = 0, c_{1s} = 0 \quad \text{for } z = 0 \quad (82)$$

For the sake of simplicity, the diffusion coefficients have been taken to be the same for both substances.

The consumption of A_1 on the electrode leads to a reduction of its concentration in the near-electrode region of the solution to a value $c_{1s} < c_1^*$. Deficiency in A_1 can be made up either by supplying this substance from the bulk of the solution, or by the formation of A_1 from A_2 via the reaction of Eq. (77). The latter is the most effective if the chemical reaction is a rapid process.

If the average lifetime of A_1 is taken to be about $1/\rho\sigma$, then the mutual transformation of substances takes place at a distance:

$$\delta_c = (D/\rho\sigma)^{1/2} \quad (83)$$

which is referred to as the reaction layer thickness.

The current recorded at the electrode is therefore caused by the reduction of A_1 from a layer of thickness δ_c :

$$i = nFDc_{1s}/\delta_c \quad (84)$$

As already pointed out, loss of the substance A_1 is replenished by delivery of A_2 to the electrode at a rate:

$$D(c_2^* - c_{2s})/\delta_d = i/nF \quad (85)$$

where c_{2s} is the concentration of A_2 in the vicinity of the electrode surface and δ_d is the diffusion boundary layer thickness. The concentrations c_{1s} and c_{2s} are interconnected by the condition of chemical equilibrium [Eq. (79)] $c_{2s} = \sigma c_{1s}$. From Eqs. (84) and (85) and the chemical equilibrium condition, the following expression is obtained for the current density at the electrode:

$$i = i_{d_2}/(1 + \sigma\delta_c/\delta_d) \quad (86)$$

where $i_{d_2} (= nFDc_2^*/\delta_d)$ is the density of the limiting diffusion current corresponding to direct reduction of substance A_2 . Since $c_2^* \gg c_1^*$, the density of the kinetic current i is much greater than the density of the limiting diffusion current i_{d_1} which would have been observed in the absence of a chemical reaction.

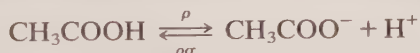
The foregoing analysis is suitable for rapid chemical reactions, when $\delta_c \ll \delta_d$ or $\rho\sigma \gg D/\delta_d^2$.

Equation (86) can easily be transformed as:

$$i\omega^{-1/2} = i_{d_2}\omega^{-1/2} - iD^{1/6}\sigma^{1/2}/(1.61\eta_0^{1/6}\rho^{1/2}) \quad (87)$$

which is frequently used in the treatment of experimental data. Equation (87), when plotted as $i\omega^{-1/2}$ against i , is a straight line (Figure 17), and the rate constant of the chemical reaction can be determined from its slope.

An example of the electrode process complicated by the preceding homogeneous monomolecular reaction is the electroreduction of H^+ ions in weak acid (say, acetic acid) solution. Equilibrium is established in the solution:



Undissociated acid molecules undergo reduction with greater difficulty than the H^+ ions. As H^+ is gradually consumed during the electrode reaction, the

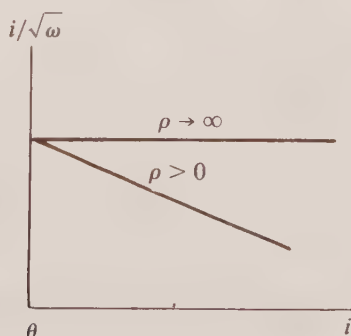


Figure 17. Scheme for the determination of the rate constant of a homogeneous chemical reaction.

equilibrium shifts to the right and the current at the electrode becomes a function of the acid dissociation rate constant ρ . Figure 18 shows the dependence of $I\omega^{-1/2}$ on I for this system. For the sake of comparison, it includes a similar plot for a strong acid (HCl) for which ρ may be taken to be infinitely great (cf., the lines a and b in Figure 18). Using the slope of the line shown in Figure 18b, Vielstich and Jahn⁽⁴⁹⁾ have determined the dissociation rate constant for acetic acid and the reverse reaction of H^+ with an anion.

The exact mathematical solution of Eqs. (80a)–(80b) with the boundary conditions of Eqs. (81)–(82) is given in Reference (7). An analysis of more complicated combinations of the chemical and electrochemical stages in electrochemical transformations may also be found in the same monograph.

8.2. Chemical Transformation of an Intermediate Product of an Electrode Process (ECE Process)

We shall now consider the influence of chemical reactions of intermediate products on the total rate of a multi-stage electrode process. Consider a process proceeding via the scheme:



The above scheme, consisting of electrochemical, chemical, and a second electrochemical stage, is often referred to as the ECE mechanism. It covers a wide range of processes encountered in real systems.

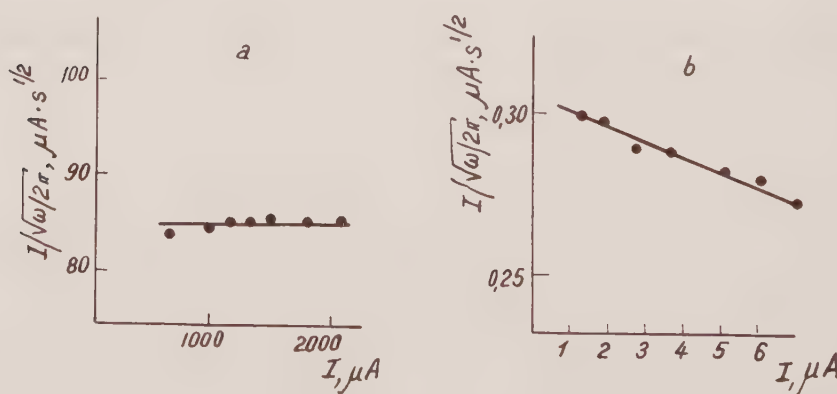


Figure 18. $I/(\omega/2\pi)^{1/2}$ vs. I for electroreduction of (a) a strong acid (HCl) and (b) a weak acid (CH_3COOH).⁽⁴⁹⁾

In determining the current i recorded at an RDE, assume, for the sake of simplicity, that both the electrochemical stages are sufficiently rapid so that the complications due to charge transfer in the reactions (88a) and (88c) may be disregarded. The diffusion coefficients will also be taken to be the same for all the substances. The current density i_1 corresponding to the reaction (88a) is equal to the density of the limiting diffusion current of the substance A_3 :

$$i_1 = n_1 F D c_3^* / \delta_d \quad (89)$$

The substance A_1 —the product of the first electrochemical stage—partly undergoes chemical reaction following Eq. (88b), being converted into an electrochemically active substance A_2 , and is partly carried away by convective diffusion into the bulk solution. For the sake of simplicity, let us assume that both these processes take place independently. We can then write the balance equation for the reacting particles A_1 :

$$i_1 / n_1 F = D c_{1s} / \delta_d + D c_{1s} / \delta_c \quad (90)$$

The first term on the right-hand side of Eq. (90) characterizes the removal of A_1 by means of convective diffusion, the second, the rate of transformation of A_1 into A_2 via reaction (88b). The quantity δ_c is the reaction layer thickness [see Eq. (83)]. It should be noted that this kind of division of the flux of A_1 is purely illustrative. In reality, the mutual interaction between convective diffusion and the chemical reaction is quite complex.

From Eq. (90) we can easily determine c_{1s} , the concentration of A_1 near the disk surface:

$$c_{1s} = (i_1 / n_1 F D) \delta_c \delta_d / (\delta_c + \delta_d) \quad (91)$$

together with the current density i_2 corresponding to the second electrochemical stage [Eq. (88c)]. This density is determined by the rate of formation of A_2 via the reaction (88c):

$$i_2 = n_2 F D c_{1s} / \delta_c = (n_2 / n_1) i_1 \delta_d / (\delta_c + \delta_d) \quad (92)$$

The density of the total current at the RDE is easily shown to be:

$$i = i_1 + i_2 = (n_1 F D c_3^* / \delta_d) [1 + (n_2 / n_1) \delta_d / (\delta_c + \delta_d)] \quad (93)$$

Rigorous calculation⁽⁷⁾ gives a slightly different expression, but the main qualitative results can be inferred from Eq. (93).

Let us introduce the concept of an effective number for electrons n_{eff} transferred in the course of the whole process:

$$n_{\text{eff}} = i \delta_d / F D c_3^* \quad (94)$$

This number characterizes the degree of homogeneous transformation of the intermediate A_1 . For the effective number n_{eff} , we may write the following

obvious inequalities:

$$n_1 \leq n_{\text{eff}} \leq n_1 + n_2 \quad (95)$$

With the help of Eq. (93) it can be shown that for a short lifetime of the intermediate, when $\delta_c \ll \delta_d$,

$$n_{\text{eff}} \approx (n_1 + n_2) - n_2(D/\rho\sigma)^{1/2}/\delta_d + \dots \quad (96)$$

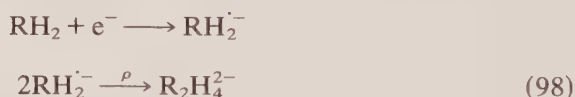
In this case, the intermediate A_1 is almost completely reduced on the disk surface.

In the case of slow transformation of A_1 , when $\delta_c \gg \delta_d$ only the first electrochemical stage is recorded at the electrode. It is accompanied by the transfer of:

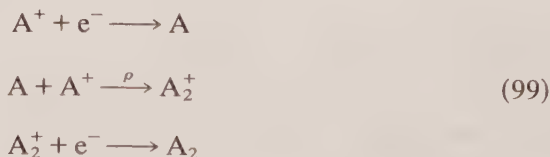
$$n_{\text{eff}} \approx n_1 + n_2\delta_d/(D/\rho\sigma)^{1/2} + \dots \quad (97)$$

electrons, whereas the stable intermediate is mainly carried away into the bulk solution. The dependence of n_{eff} on δ_d (i.e., on $\omega^{1/2}$ in the end) serves as a criterion for determining $\rho\sigma$. The calculations made in a number of papers (see Reference 7) for a system with an ECE mechanism are, in general, purely illustrative. In practice, however, it is not possible to simplify the mathematical problem sufficiently to obtain a general solution in an analytical form. The diffusion equations must therefore be solved numerically and the dependence $n_{\text{eff}} = F(\omega)$ is obtained in the form of graphs, where the rate constant of the chemical stage ($\rho\sigma$) serves as a parameter. By comparing the calculated and experimental curves for n_{eff} vs. $\log c_3^*\omega^{-1}$, as shown in Figure 19,⁽⁵⁰⁾ the value of ρ may be determined (since D , c_3^* and σ are known).

Using this method, Adams⁽⁵¹⁾ and Nigrette and Bard⁽⁵²⁾ have studied a series of reactions of organic compounds, electrohydrodimerization, in particular:



and electrodimmerization:



From the above, it follows that the RDE method may be used in studying a wide range of often complicated electrode processes. Certain different cases of these processes, for example, diffusion or mixed kinetics in the electro-

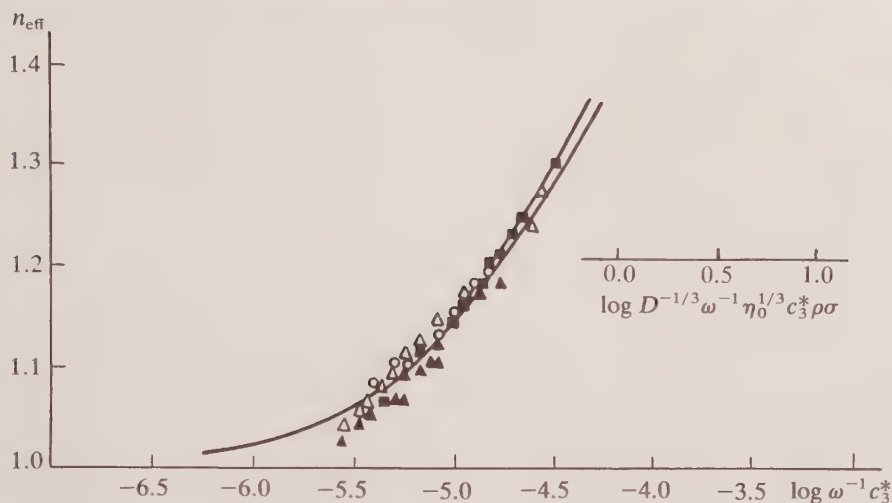


Figure 19. Determination of the rate constant of the chemical stage in the ECE process of electrooxidation of acetyltriphenylamine.⁽⁵⁰⁾ Solid lines: computer calculation (n_{eff} vs. $\log D^{-1/3} \omega^{-1} \eta_0^{1/3} c_3^* \rho \sigma$, see upper scale); points: experimental results for different concentrations of acetyltriphenylamine (n_{eff} vs. $\log \omega^{-1} c_3^*$).

chemical stage, presence of chemical homogeneous or heterogeneous stages, or different orders of individual stages with respect to reagent concentration are characterized by specific types of dependence of the current on different variables. These include electrode rotation speed, reagent concentration, potential and temperature. The dependence of the half-wave potential on the rotation speed and other criteria may be used. On undertaking a study of a new system, the investigator is frequently unable to visualize the detailed reaction mechanism and the kinetic characteristics of its individual stages. In such cases, it is convenient to make use of a system of sequential tests⁽⁵³⁾ which makes it possible to determine the detailed scheme of the process and to investigate its kinetics by recording the characteristic dependence of the quantities quoted above on the experimental parameters, as measured by the RDE technique.

9. Rotating Ring-Disk Electrode

9.1. Qualitative Description

A rotating ring-disk electrode (RRDE, Figure 20) consists of three elements: central disk electrode D (of radius r_{10}), ring electrode R (of inner radius r_{20} and outer radius r_{30}) and a thin insulating spacer G of thickness $r_{20} - r_{10}$ which separates the disk and ring electrodes. The working surfaces

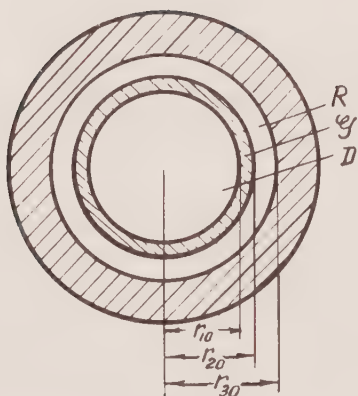


Figure 20. A scheme of the ring-disk electrode.

of both the electrodes and the spacer surface lie in one plane, thereby forming a planar surface. The whole system is in rotary motion about its axis. Each electrode is an independent entity, i.e., its potential (or the current) is monitored independently.

In order to illustrate the physical principles underlying the RRDE method, let us consider a two-stage electrode reaction occurring on the central disk electrode:



The intermediate product B formed during the reduction of A via the reaction (100a) can be further reduced via the reaction (100b), thus, leading to the final product P_2 . If the rate of the reaction (100b) is not sufficiently high, it is clear that part of the intermediate product B will not be able to participate in this reaction, but will be entrained by the flow of liquid along the electrode surface (cf., Figure 1). If a second electrode (the ring) which is capable of detecting the substance B with the help of a suitable electrochemical reaction is placed in the convective pathway, then there is a possibility of determining the amount of B that has not entered into the reaction (100b), and thus to establish the reaction rate constant.

In order to estimate the quantitative characteristics of the RRDE, we must first calculate or empirically determine its collection efficiency, i.e., to find out the fraction of a stable substance generated on the disk (D) that may be collected on the ring electrode (R) for a given radii of the disk and the ring. It is also necessary to elucidate the way in which the current recorded on the ring is related to the electrode rotation speed and the kinetics of the electrochemical reaction on the disk.

9.2. Collection Efficiency of the RRDE

In order to calculate the collection efficiency N , a subsidiary problem may be first considered.

Let us assume that the rate of formation of the intermediate B is not uniform over the disk surface, but varies as a certain function of the distance from the rotation axis. In other words:

$$D_B \left(\frac{\partial c_B}{\partial z} \right)_s = i_1(r) / n_2 F \quad \text{for } z = 0, r \geq 0 \quad (101)$$

where c_B is the concentration of the intermediate, and $i_1(r)$ is the local value of the current density corresponding to Eq. (100a).

The intermediate B is carried away by the moving liquid into the bulk solution. We will now determine the distribution of the intermediate over the disk surface caused by the current $i_1(r)$. As a result of axial symmetry, the equation of convective diffusion (see Section 3) is of the form:

$$v_r \frac{\partial c_B}{\partial r} + v_z \frac{\partial c_B}{\partial z} = D_B \frac{\partial^2 c_B}{\partial z^2} \quad (102)$$

According to Eq. (5), the radial and axial components of the liquid velocity near the disk surface are:

$$v_r \approx a_0 r \omega (\omega / \eta_0)^{1/2} z \quad (103a)$$

$$v_z \approx -a_0 (\eta_0 \omega)^{1/2} (\omega / \eta_0) z^2 \quad (103b)$$

There is no intermediate B in the bulk of the solution, hence:

$$c_B \rightarrow 0 \text{ as } z \rightarrow \infty, r \geq 0 \quad (104)$$

As demonstrated in References (7) and (54), after the introduction of the new variables:

$$\xi = (a_0 \omega^{3/2} / 2 \eta_0^{1/2})^{1/2} r z \quad \text{and} \quad \zeta = (2 a_0 \omega^{3/2} / 9 \eta_0^{1/2})^{1/2} r^3$$

Equation (102) reduces to a diffusion equation of a simpler type:

$$\frac{\partial c_B}{\partial \zeta} = \frac{D_B}{4 \xi} \frac{\partial^2 c_B}{\partial \xi^2}$$

Its solution can be represented in a comparatively simple form. In particular, with the boundary conditions (101) and (104), the following relationship can be obtained for the concentration c_{Bs} of the intermediate B over the disk surface (for $z = 0$):

$$c_{Bs} = - \frac{3 \delta_d}{n_2 F D_B \Gamma(1/3) \Gamma(2/3)} \int_0^r \frac{i_1(\rho) \rho d\rho}{(r^3 - \rho^3)^{2/3}} \quad (105)$$

The usual radial variable r has been used in writing this equation. From Eq. (105) it can be seen that the distribution of the intermediate B over the disk surface depends on the rate of generation of B on the electrode. The equation can be applied in an analysis of current distribution in an RRDE system.

As shown in Section 3, formation of the intermediate B on the surface of the disk electrode B takes place at a uniform rate at all points:

$$i_1 = \text{const.} \quad \text{for } r \leq r_{10} \quad (106)$$

The relationship for the concentration of the substance B on the disk surface $c_{Bs} = i_1 \delta_d / n_2 F D_B$ can be derived directly from Eq. (105).

There is no current on the surface of the insulating gap G, i.e.:

$$i_1 = 0 \quad \text{for } r_{10} < r \leq r_{20} \quad (107)$$

The intermediate is detected on the ring electrode R. We shall assume that the electrochemical reaction used for this purpose, say, oxidation of B:



takes place in a purely diffusion regime with the transfer of n_R electrons. (The reaction mechanism on the ring electrode and the number n_R are considered to be known.) Thus:

$$c_{Bs} = 0 \quad \text{for } r > r_{20} \quad (109)$$

The current density of oxidation of B on the ring electrode i_R is related to i_1 in Eq. (105) as follows:

$$i_R = -(n_R/n_2)i_1 \quad \text{for } r > r_{20} \quad (110)$$

where the minus sign indicates that the current on the ring is in the opposite direction to that on the disk.

Substituting Eqs. (106), (107), (109), and (110) into Eq. (105), we obtain an integral equation for the current on the ring electrode:

$$\frac{n_2}{n_R} \int_{r_{20}}^r \frac{i_R \rho \, d\rho}{(r^3 - \rho^3)^{2/3}} = i_1 \int_0^{r_{10}} \frac{\rho \, d\rho}{(r^3 - \rho^3)^{2/3}} \quad \text{for } r > r_{20} \quad (111)$$

Its solution, as shown in Reference (54), is of the form:

$$i_R = i_1 \left(\frac{n_R}{n_2} \right) \left\{ \frac{r}{(r^3 - r_{20}^3)^{1/3}} G \left(\frac{r_{10}^3}{r_{20}^3 - r_{10}^3} \right) - G \left[\frac{(r^3 - r_{20}^3)}{(r_{20}^3 - r_{10}^3)} \cdot \frac{r_{10}^3}{r^3} \right] \right\} \quad \text{for } r > r_{20} \quad (112)$$

The function $G(z)$ of the corresponding argument in Eq. (112) is defined as follows:

$$G(z) = \frac{3^{1/2}}{2\pi} \int_0^z \frac{d\zeta}{\zeta^{1/3}(1+\zeta)} \\ = \frac{3^{1/2}}{4\pi} \ln \frac{1+z}{(1+z^{1/3})^3} + \frac{3}{2\pi} \arctan \frac{2z^{1/3}-1}{3^{1/2}} + \frac{1}{4} \quad (113)$$

In the RRDE method, the total current:

$$I_R = 2\pi \int_{r_{20}}^{r_{30}} i_R r dr$$

is recorded on the ring electrode.

On substituting Eq. (112) in the integrand, we obtain [see Reference (54)]:

$$I_R = I_D(n_R/n_2)N \quad (114)$$

where:

$$N = \left(\frac{r_{30}^3 - r_{20}^3}{r_{10}^3} \right)^{2/3} G \left(\frac{r_{10}^3}{r_{20}^3 - r_{10}^3} \right) + G \left(\frac{r_{30}^3 - r_{20}^3}{r_{20}^3 - r_{10}^3} \right) \\ - \left(\frac{r_{30}^3}{r_{10}^3} \right)^{2/3} G \left[\left(\frac{r_{10}^3}{r_{20}^3 - r_{10}^3} \right) \left(\frac{r_{30}^3 - r_{20}^3}{r_{30}^3} \right) \right] \quad (115)$$

is the collection efficiency, which quantitatively characterizes the mutual influence of the disk and the ring electrodes, and $I_D = \pi r_{10}^2 i_1$ is the total current on the disk electrode.

From the form of relationship (114), it may be concluded that the current I_R on the ring electrode is proportional to the current I_D on the disk, i.e., the rate at which the intermediate B is formed. According to Eq. (115), the RRDE efficiency N is exclusively dependent on the geometric parameters, and does not depend on the rotation speed ω . The value of N has been calculated in References (6) and (7) for a wide range of these parameters (see Table 1⁽⁶⁾). N varies from 0.2 to 0.4 in the majority of practical cases.

For the approximate calculation of N , the following formula⁽⁵⁵⁾ can be used:

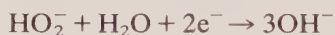
$$N = \left(\frac{r_{30}^3 - r_{20}^3}{r_{20}^3 - r_{10}^3} \right)^{2/3} \left[\frac{1}{2.44 + \left(\frac{r_{10}^3}{r_{20}^3 - r_{10}^3} \right)^{2/3}} \right. \\ \left. + \frac{1}{2.44 + \left(\frac{r_{30}^3 - r_{20}^3}{r_{20}^3 - r_{10}^3} \right)^{2/3}} - \frac{1}{2.44 + \left(\frac{r_{10}^3}{r_{30}^3} \cdot \frac{r_{30}^3 - r_{20}^3}{r_{20}^3 - r_{10}^3} \right)^{2/3}} \right] \quad (115a)$$

Table 1
Collection Efficiency of RRDE^a

r_{30}/r_{20}	r_{20}/r_{10}								
	1.02	1.03	1.04	1.05	1.06	1.07	1.08	1.09	1.10
1.02	0.1013	0.0976	0.0947	0.0922	0.0902	0.0884	0.0869	0.0855	0.0843
1.03	0.1293	0.1250	0.1215	0.1186	0.1162	0.1140	0.1121	0.1104	0.1089
1.04	0.1529	0.1483	0.1444	0.1412	0.1385	0.1360	0.1339	0.1320	0.1302
1.05	0.1737	0.1687	0.1647	0.1612	0.1582	0.1556	0.1533	0.1512	0.1483
1.06	0.1923	0.1872	0.1829	0.1793	0.1761	0.1733	0.1708	0.1686	0.1665
1.07	0.2092	0.2039	0.1996	0.1958	0.1925	0.1896	0.1869	0.1846	0.1824
1.08	0.2247	0.2194	0.2149	0.2110	0.2076	0.2046	0.2019	0.1994	0.1972
1.09	0.2392	0.2338	0.2292	0.2252	0.2217	0.2186	0.2158	0.2133	0.2110
1.10	0.2526	0.2412	0.2426	0.2385	0.2350	0.2318	0.2289	0.2263	0.2240
1.12	0.2772	0.2717	0.2670	0.2629	0.2593	0.2560	0.2530	0.2503	0.2479
1.14	0.2992	0.2938	0.2890	0.2849	0.2812	0.2778	0.2748	0.2720	0.2695
1.16	0.3192	0.3138	0.3090	0.3048	0.3011	0.2977	0.2947	0.2919	0.2893
1.18	0.3375	0.3321	0.3274	0.3232	0.3154	0.3161	0.3130	0.3101	0.3075
1.20	0.3544	0.3490	0.3443	0.3402	0.3364	0.3330	0.3290	0.3271	0.3245
1.22	0.3701	0.3648	0.3601	0.3560	0.3523	0.3489	0.3458	0.3429	0.3403
1.24	0.3848	0.3795	0.3749	0.3708	0.3671	0.3637	0.3606	0.3577	0.3551
1.26	0.3985	0.3933	0.3887	0.3847	0.3810	0.3776	0.3745	0.3717	0.3691
1.28	0.4115	0.4063	0.4018	0.3977	0.3941	0.3907	0.3877	0.3849	0.3822
1.30	0.4237	0.4186	0.4141	0.4101	0.4065	0.4032	0.4001	0.3973	0.3947
1.32	0.4353	0.4302	0.4258	0.4218	0.4183	0.4150	0.4119	0.4092	0.4066
1.34	0.4463	0.4413	0.4369	0.4330	0.4294	0.4262	0.4232	0.4204	0.4278

^a From Reference 6.

By way of illustration, Figure 21a shows the polarization curve of the electroreduction of molecular oxygen on an amalgamated copper disk (the next section is devoted to a study of this reaction). In alkaline solution, this reaction proceeds in two stages:



and two waves in the polarogram correspond to these stages.

In the potential range of the first wave, hydrogen peroxide is stable on mercury and may accumulate in the solution. In the potential range of the second wave, however, it suffers reduction and is thus a reaction intermediate. Hydrogen peroxide may undergo oxidation (or reduction) on a gold ring (see Figure 21b), and thus reveal its formation as an intermediate. Using the ratio of currents on the ring and the disk electrodes (in the first wave potential range) the RRDE efficiency N can be determined. In this and other systems, experimental determination of N has demonstrated the quite satisfactory accuracy of the RRDE theory.

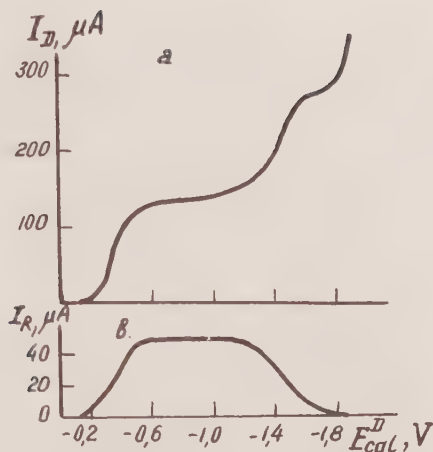


Figure 21. Cathode reduction of oxygen in 0.01 *N* NaOH⁽³⁾: (a) polarization curve on an amalgamated disk; (b) limiting current of HO₂⁻ oxidation on gold ring vs. disk potential.

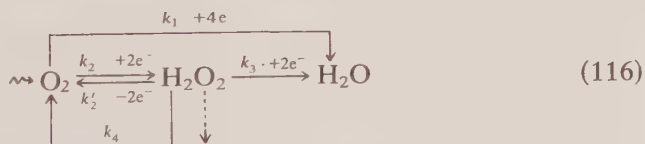
It should be borne in mind that non-uniform polarization of the RRDE, say, in solutions of high ohmic resistance may give rise to perceptible errors in applying the RRDE technique. On the other hand, this method may be applied to control the homogeneity of current distribution on the disk electrode surface.

9.3. Investigation of Multi-Stage Processes

9.3.1. Reduction of Molecular Oxygen

This reaction is a complicated electrode process which proceeds in several parallel and consecutive stages. Investigation of the reduction of oxygen by means of the RRDE method is, in a certain sense, the culmination of the practical applications of the method and clearly illustrates its potentialities. The scheme for analyzing other, simpler electrode processes may be constructed by simplifying the scheme for oxygen reduction. At the same time, the limitations inherent in the RRDE method in its classical version are clearly seen in an example of the analysis of the process.

The general scheme of reactions taking place during oxygen ionization can be conveniently represented as follows (see also Chapter 6 of Volume 7):



Molecular oxygen, whose concentration shall be denoted by c_A , may undergo reduction simultaneously via two reactions: directly to water (or to

OH in alkaline solutions) with the consumption of four electrons (rate constant k_1) or to hydrogen peroxide with the consumption of two electrons (rate constant k_2). Hydrogen peroxide, whose concentration shall be denoted by c_B , may further be reduced to water (rate constant k_3), or may be subjected to catalytic decomposition, which in turn may proceed in two ways: electrochemical decomposition with a rate constant of k'_2 and a non-electrochemical decomposition with a rate constant of k_4 .

The dotted arrow in the scheme (116) indicates that, depending on the relationship between the rate constants k_2 , k'_2 and k_3 , a certain part of hydrogen peroxide generated may not be reduced at the electrode and may diffuse into the bulk of the solution. It is precisely this hydrogen peroxide that is detected on the ring electrode, and thus it provides a means of studying the whole of process (116). The wavy arrow in scheme (116) indicates the supply of molecular oxygen to the electrode surface.

Scheme (116) may be regarded as a nominal one. On the one hand, it is sufficiently general and covers most of the cases encountered in practice. On the other hand, it is sufficiently simple to allow determination of the rate constants of all five stages in a single RRDE experiment, as will be shown below.

If necessary, additional complications may be incorporated in the scheme. Thus, Tarasevich⁽⁵⁷⁾ has pointed out the need to account for the slow H_2O_2 desorption and the dissociative adsorption of oxygen [in the scheme (116) it is assumed that all the adsorption equilibria are established very rapidly, and in addition, the condition of first order in all stages of the process is not violated].

Now we shall write the equations of material balance which describe the variation in the concentrations of molecular oxygen and hydrogen peroxide at the disk electrode:

$$D_A(c_A^* - c_{As})/\delta_{dA} = (k_1 + k_2)c_{As} - (k'_2 + k_4/2)c_{Bs} \quad (117a)$$

$$k_2c_{As} = (k_3 + k_4 + k'_2)c_{Bs} + (D_Bc_{Bs}/\delta_{dB}) \quad (117b)$$

The left-hand side of Eq. (117a) shows that oxygen is delivered from the bulk of the solution to the electrode surface by convective diffusion, while the right-hand side indicates consumption and formation of oxygen as a result of the reactions taking place at the electrode. Equation (117b) for hydrogen peroxide has also been derived in similar manner. Here, δ_{dA} and δ_{dB} stand for the thicknesses of the diffusion boundary layers of the corresponding reagents.

The total current I_D measured at the disk electrode is the result of all the charge transfer reactions in scheme (116):

$$I_D = \pi r_{10}^2 F [4k_1 + 2k_2]c_{As} + (2k_3 - 2k'_2)c_{Bs}] \quad (118)$$

The diffusion flow of hydrogen peroxide from the disk surface is:

$$J = \pi r_{10}^2 D_B c_{Bs} / \delta_{dB} \quad (119)$$

As already demonstrated in Section 9.2, part of this flow, which depends on the RRDE efficiency N , can be collected at the ring electrode. If two electrons ($n_R = 2$) are transferred in the reaction of hydrogen peroxide at the electrode, the total current I_R recorded at the ring will be:

$$I_R = 2\pi r_{10}^2 F N D_B c_{B_s} / \delta_{dB} \quad (120)$$

After solving Eqs. (117a) and (117b) for c_{A_s} and c_{B_s} , and then substituting the values thus found in Eqs. (118) and (120), we may obtain expressions for I_D and I_R .

As pointed out above, all the reactions contained in the general scheme (116) are of the first order. In Section 6.1, it was noted that a convenient method of determining the kinetic parameters of first order reactions is extrapolation of the experimental data to $\omega \rightarrow \infty$. In such an extrapolation, it is possible to obtain the "true" kinetic current not distorted by concentration polarization. A similar approach may also be used in the RRDE technique. In contrast to the RDE method, however, some special combinations of experimental values of measured currents are extrapolated. On the basis of direct calculations we can easily show that⁽⁷⁾:

$$\frac{I_D}{I_R} = \left\{ \frac{2k_1 + k_2}{k_2} + \left[\frac{(2k_1 + k_2)(k_3 + k'_2 + k_4)}{k_2} + (k_3 - k'_2) \right] \frac{\gamma_B}{D_B \omega^{1/2}} \right\} N^{-1} \quad (121a)$$

and

$$\frac{(I_{dA} - I_D)}{I_R} = \left\{ 1 + 2 \left[\frac{(k_3 + k'_2 + k_4)}{k_2} \cdot \frac{D_A \gamma_B}{D_B \gamma_A} \right] + \frac{2D_A \omega^{1/2}}{k_2 \gamma_A} \right\} N^{-1} \quad (121b)$$

where:

$$\gamma_A = 1.61 D_A^{1/3} \eta_0^{1/6} \quad \text{and} \quad \gamma_B = 1.61 D_B^{1/3} \eta_0^{1/6}$$

and $I_{dA} = 4F\pi r_{10}^2 D_A c_A^* / \delta_{dA}$ is the total limiting diffusion current of oxygen reduction. A ratio of the type of Eq. (121a), indeed, for a simpler case than that of the complete scheme (116), was suggested by Bockris *et al.*,⁽⁵⁸⁾ and the "double extrapolation" of Eqs. (121a)–(121b) was introduced by Bagotzky *et al.*⁽⁵⁹⁾ Müller and Nekrasov⁽⁶⁰⁾ were the first to use the RRDE method in a quantitative analysis of oxygen ionization reaction.

It can readily be seen that the ratio of Eq. (121a) is a linear function in $I_D/I_R - 1/\omega^{1/2}$ coordinates, while that of Eq. (121b) is linear in $(I_{dA} - I_D)/I_R - \omega^{1/2}$ coordinates. The slope of these lines and the intercepts on the ordinate axis are determined by the combinations of the rate constants of the partial reactions of the overall process. Thus, the plots constructed in these coordinates may be used in determining the rate constants of the scheme (116).

Double extrapolation provides a means of determining four of the individual rate constants contained in a scheme of this type or their

combinations from the four quantities derived from experimental curves (two slopes and two intercepts on the ordinate axis). If, however, there are five reaction stages as in the complete scheme (116), Eqs. (121a) and (121b) are not sufficient to determine all five rate constants, and then other relationships have to be used (for example, the thermodynamic relationship between k_2 and k'_2 in terms of the reversible potential of the system O_2/H_2O_2 , assuming it to be an equilibrium). If, however, the scheme of the electrode process under investigation is simpler than scheme (116), then, assuming that the rate constants of the "missing" stages are zero, we can easily derive the necessary relationships for the analysis from Eqs. (121a) and (121b).

In order to illustrate the above approach, let us consider a version of scheme (116) in which there is no oxidation or decomposition of hydrogen peroxide, i.e., $k_4 = k'_2 = 0$. Then, as is obvious from Eq. (121a), an I_D/I_R vs. $\omega^{-1/2}$ graph will be of the form shown in Figure 22. If direct reduction of oxygen to water does not take place ($k_1 = 0$), and hydrogen peroxide is stable on the disk and is not reduced further ($k_3 = 0$), then a line parallel to the abscissa (a) is obtained in $I_D/I_R - \omega^{-1/2}$ coordinates. If, however, hydrogen peroxide undergoes further reduction, then, depending on the disk potential, k_3 varies and the line has a different slope (b). If both the parallel processes of oxygen reduction (reduction to hydrogen peroxide and reduction to water) take place simultaneously, but hydrogen peroxide does not undergo further reduction ($k_3 = 0$), then several lines parallel to the abscissa (c) are obtained, and the intercepts on the ordinates depend on the ratio of the rate constants

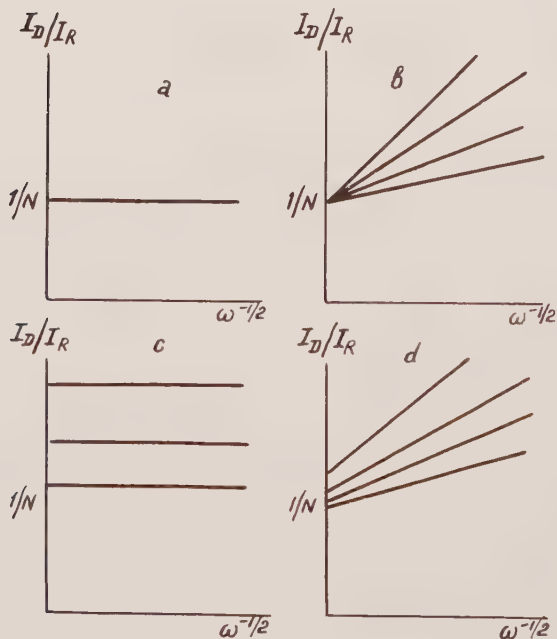


Figure 22. A scheme for graphic analysis of oxygen ionization data.⁽⁶⁸⁾ Different lines on the graphs pertain to different disk electrode potentials (see text for the explanation of Figures a to d).

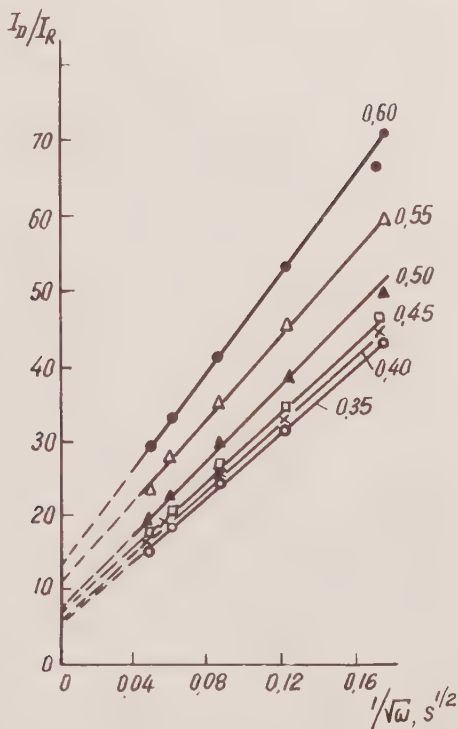


Figure 23. Graphic analysis of data pertaining to oxygen ionization on Pt electrode in an alkaline solution.⁽⁵⁸⁾ Disk electrode potential is shown on lines (in volts).

k_1/k_2 . This ratio, in general, will depend on the potential. Finally, Figure 22d shows the general case where k_1 , k_2 and k_3 are all different from zero.

The experimental results in Figure 23 (cf., Figure 22d) are shown here for the sake of illustration, without considering the detailed evaluation of oxygen reduction. A summary of the results obtained by the RRDE method is given in References (7) and (10).

9.3.2. Anodic Dissolution of Multivalent Metals and Reduction of Their Ions

The RRDE method has been used to detect ions of intermediate valency and to measure their kinetic parameters of formation and further reaction. The analytical procedure does not differ in principle from that discussed in the previous section.

As an example, a typical scheme for the two-stage reduction of bivalent metal ions can be written as follows:



Using the same procedure as above, the following relationship can be easily

derived:

$$I_D/I_R = (1 + 2k_3\gamma_B/D_B\omega^{1/2})/N \quad (123a)$$

$$(I_{dA} - I_D)/I_R = [1 + 2D_A\gamma_A k_3/D_B\gamma_B k_2) + (2D_A\omega^{1/2}/k_2\gamma_A)]/N \quad (123b)$$

where the index "A" pertains to Me^{2+} ions and "B" to the intermediate Me^+ . I_{dA} is the limiting diffusion current for complete reduction of Me^{2+} . It is also assumed that Me^+ ions are detected at the ring electrode by means of their oxidation back to the initial Me^{2+} . Detection of unstable Be^+ , an intermediate in the anodic dissolution of beryllium, is an example of application of the method. The lifetime of this ion is estimated in the range from 10^{-1} to 10^{-2} s.⁽⁶¹⁾

A more complicated example is the anodic dissolution of indium (and the cathodic reduction of In^{3+} ions), where intermediates, in principle, may prove to be In^{2+} along with In^+ . In such situations an electrode in the form of a rotating disk with a split ring⁽⁶²⁾ is a convenient tool in determining the valency of the intermediate. A ring cut off at its diameter becomes two independent electrodes, each with its own current lead. The potential of one of the half-rings is preset in the range of the limiting current of the intermediate product oxidation, while the potential of the second half-ring remains in the range of the reduction of the intermediate. The ratio of the currents at the half-rings (for a given current of the disk) allows determination of the number n of electrons participating in the corresponding reactions, and consequently, the valency of the intermediate.

The RRDE method has been applied to investigate the dissolution and corrosion of metals and to study the dissolution kinetics of non-metallic substances (for example, poorly soluble salts) [see Reference (7)].

9.3.3. Reactions of Organic Compounds

The potential advantages of the RRDE method have been demonstrated most clearly in studies of the mechanism of electrochemical reactions of organic compounds characterized by a diversity of parallel paths and intermediate stages. Identification of the intermediates formed has been via the shapes of polarization curves recorded at the ring electrode. In particular, the waves observed at the ring have been compared, by the value of the half-wave potential and by the number of electrons, to the waves of the known substances which may be postulated as intermediates in the reactions under study.

This may be illustrated by the investigations of the reduction of aromatic aldehydes and ketones.⁽⁶⁴⁾ Benzaldehyde, benzophenone, acetophenone, and similar compounds yield a series of products during reduction on an amalgamated gold disk electrode. Among them are the unstable ion-radicals (lifetime 10^{-2} – 10^{-3} s).

9.3.4. Homogeneous Chemical Reactions of Intermediates

The RRDE theory described above is applicable to stable or relatively long-lived intermediates. If, however, the intermediates are unstable and suffer partial decomposition in the course of movement from the disk electrode to the ring, thereby passing into an electrically inactive form, certain modifications have to be introduced into the above equations for analyzing electrochemical processes.

First, the RRDE collection efficiency N_c for unstable intermediates is less than the corresponding value N for stable particles. A decrease in the efficiency depends on the rate constant ρ of the chemical conversion in the near-electrode solution layer and, to a first approximation⁽⁷⁾ may be given by the following expression:

$$N_c = N(1 - b_1 \delta_d^2 / \delta_c^2 + \dots) \quad (124)$$

where δ_c is the thickness of the reaction layer corresponding to the decomposition of the intermediate [cf., Eq. (83)]. The value of b_1 depends on the geometrical dimensions of the disk and the ring. As can be seen from Eq. (124), the value of N_c , unlike N , is dependent on the disk rotation speed (because $\delta_d^2 \sim \omega^{-1}$).

The dependence of N_c on the rotation speed ω is an important factor in studying the unstable intermediates by the RRDE method. Computer-aided calculations⁽⁶⁵⁾ of N_c provide a means of obtaining information on the mechanism and kinetics of homogeneous chemical reaction of the intermediate, by comparison of the experimental and calculated values of N_c . The ring-disk method, along with mathematical simulation, is currently being successfully applied to the study of the reactions of organic compounds which proceed via the ECE scheme (cf., Section 8.2).

9.4. Investigation of Adsorption

In the investigations presented in the previous pages, adsorption of the reagents at the electrode and desorption of the products of the electrode reactions were not in general taken into consideration. In real systems, however, adsorption equilibrium is often established quite slowly, and the kinetics of the stages of adsorption and desorption has a marked, if not decisive, influence on the kinetics of the process as a whole. Owing to the influence of adsorption kinetics on the currents measured at the disk and the ring, the RRDE method has been proposed for measuring the magnitude of adsorption.⁽⁶⁶⁾

Let the potential of a disk electrode E_D be chosen so that substance A in the solution may be adsorbed on the electrode but does not enter into any electrochemical reaction. After the establishment of the adsorption equilibrium, the disk potential is linearly swept from its initial value to a certain final

value, at which the oxidation reaction:



takes place. The reaction product B is completely or partially desorbed from the disk. The ring electrode potential is chosen, so that the reverse reaction of Eq. (125) (i.e., reduction of B) takes place on the ring.

The specific features of the adsorption stages of reaction (125) determine the qualitative pattern of the potentiodynamic curve at the disk electrode and the ring current vs. the disk potential, which are schematically shown in Figure 24. Curve 1 represents the usual I_D - E_D curve when the substances A and B are not adsorbed. Curve 3 is the corresponding ring electrode plot. Curve 2 at the disk electrode is typical of oxidation of a substance from an adsorbed layer. In this case, curve 4 (A is more strongly adsorbed than B) or curve 5 (adsorption of B exceeds that of A) is obtained on the ring.

Another method which has been examined is nonstationary and is based on measuring the transition time characterizing the rate of the convective diffusion disk-to-ring mass transfer. It is appropriate to emphasize here that the application of nonstationary polarization to the disk electrode opens up interesting possibilities for investigating the intermediates of electrode processes by means of the RRDE method. It should, however, be pointed out that such techniques are mostly qualitative estimates, since a rigorous quantitative description of the processes of nonstationary convective diffusion in RRDE method leads to considerable mathematical difficulties. If the disk potential is changed stepwise, the change in the current flowing will be recorded at the

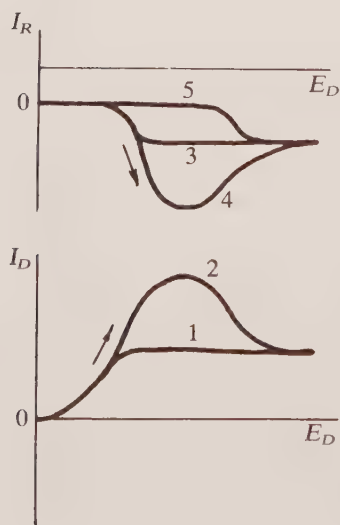


Figure 24. Schematic representation of potentiodynamic curves on disk electrode and curves of ring electrode current recorded in adsorption studies by means of the RRDE technique.⁽⁶⁶⁾

ring electrode after the lapse of a certain time interval. This change is caused by the change in the composition of the near-electrode solution layer. The delay between the perturbation at the disk and the signal at the ring is due to the finite rate of transfer of the reagents from the disk to the ring. The time for a substance formed near the surface of a disk of radius r_{10} to reach the inner boundary of a ring of radius r_{20} has been estimated in Reference (67) under the assumption that the substance moves simultaneously in two directions, by diffusion along the electrode plane and by transfer in the radial direction along with the solution. Neglecting the convective transfer along the rotation axis, we obtain the following estimate for the time delay τ_R :

$$\tau_R m = 43.1(\eta_0/D)^{1/3}[\log(r_{20}/r_{10})]^{2/3} \quad (126)$$

where m is the electrode rotation speed (rpm). Where the reaction product is desorbed from the electrode surface at a slow rate, the time interval between the change in the disk potential and the ring response is increased compared to the value calculated by Eq. (126).

Both the above methods have been extensively applied by Bruckenstein and others in studying the chemisorption of metal ions on electrodes (so-called underpotential deposition).

Symbols List

c^*	bulk concentration
c_s	concentration in the vicinity of the disk surface
c_O, c_R	concentration of the oxidized or reduced form, respectively
D	diffusion coefficient
f	frequency of the harmonic signal
F, G, H	dimensionless functions (see Eq. 1)
i	current density
i_d	diffusion limiting current density
i_{dO}, i_{dR}	diffusion limiting current density of oxidized or reduced form, respectively
i_k	kinetic current density
i_0	exchange current density
I	total current at the electrode
I_d	total diffusion limiting current
I_D, I_R	total current to the disk or ring electrode, respectively
j	flux density of the dissolved species to the electrode
k	rate constant of the heterogeneous process
k_f, k_b	rate constants of the forward and backward reactions respectively
m	number of disk revolutions per minute
N	collection efficiency of RRDE

r	radial axis
r_0, r_{10}	radius of the rotating disk electrode
r_{20}, r_{30}	internal and external radii of the rotating ring, respectively
R	gas constant
Re	$= \omega r_0^2 / \eta_0$ = dimensionless Reynolds number
S	surface area of the disk
$Sc = \eta_0 / D$	dimensionless Schmidt number
t	time
T	absolute temperature
$\vec{V}$	vector of the liquid velocity
V_r, V_φ, V_z	radial, azimuthal, or normal component of $\vec{V}$, respectively
z	axis normal to the disk surface
α	transfer coefficient
	$= 3.6\sqrt{\eta_0/\omega}$ = thickness of the hydrodynamic boundary layer
δ_d	$= 1.61 D^{1/3} \eta_0^{1/6} \omega^{-1/2}$ = thickness of the diffusion layer according to Levich
δ_c	$= \sqrt{D/\rho\sigma}$ = thickness of the reaction layer
η	overpotential
η_0	kinematic viscosity
μ	reaction order of the heterogeneous process
ρ	rate constant of the chemical reaction in the bulk
σ	chemical equilibrium constant
ω	angular velocity of the disk

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6

Thin Layer Cell Techniques

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1. Introduction

Thin layer electrochemical techniques have proven in many studies to be an attractive alternative to conventional semi-infinite methods. The attractiveness of thin layer cells usually stems from the fact that the reactant solution is kept within 10^{-3} to 10^{-2} cm of the working electrode. As a result of this special geometry a number of benefits are reaped, including simpler descriptive equations, cleaner electrode surfaces, and more rapid exhaustive electrolysis.

In the United States, this field of electrochemistry began in 1961 as a fortunate mistake. Anson⁽¹⁾ reported that he had observed the adsorption of iron(II) and iron(III) on a platinum wire electrode. This seemed to be a valid deduction since when the electrode was removed from the reactant solution, washed, and then inserted into a fresh solution of supporting electrolyte, chronopotentiograms which indicated the continued presence of iron were obtained. However, later that same year Anson⁽²⁾ pointed out that this was not the case at all. In fact, what he had observed was the electrochemistry of reactant solution caught in the tiny crevices between the platinum wire electrode and the glass tube in which one end of the electrode was sealed. Two years later, in 1963, Christensen and Anson⁽³⁾ reported the first U.S. application of the thin layer technique: an n -value determination. This time the thin layer cell was of more intentional design.

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Actually two other thin layer applications were published in Europe slightly prior to Christensen and Anson's 1963 publication.⁽³⁾ Schmidt and Gygax⁽⁴⁾ designed what they called a "chamber electrode" and employed it in metal deposition studies. The second application, which was reported by Sluyters,⁽⁵⁾ dealt with the determination of a.c. impedances across thin layers of solution.

At best, this chapter is only an introductory survey of the rapidly expanding field of thin layer electrochemistry. A wealth of additional information is available from other sources, including two reviews,^(6,7) and a chapter in *Electroanalytical Chemistry*.⁽⁸⁾

2. Theory

The model (Figure 1) used for the theory presented here is a thin layer of solution ($2\text{--}50\ \mu$) bounded by two parallel working electrodes and connected to the reference and auxiliary electrodes via a salt bridge.

The theory associated with a thin layer electrode is relatively simple if one important criterion is met: diffusional mass transfer of the electroactive species to the working electrode, due to their close proximity, is essentially instantaneous, thereby rapidly establishing the appropriate concentration profiles in the thin layer. When this simplifying assumption can be made (i.e., the thin layer condition holds), the actual geometry of the cell does not affect the form of the descriptive equations. However, to determine what experimental conditions are necessary to justify this simplification, equations which include diffusion terms must be derived and compared to those obtained when diffusion is ignored. Since to develop equations including diffusional terms requires solving Fick's second law, some knowledge of the cell's geometry is needed to determine the appropriate boundary conditions. In those derivations the model described above is generally employed.

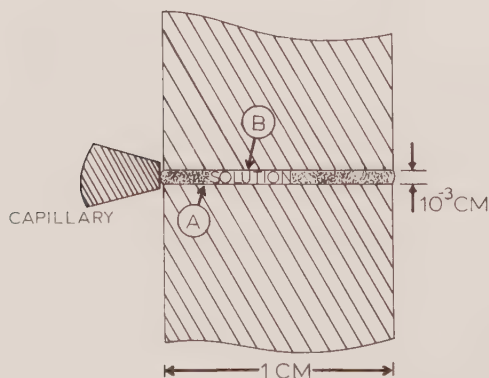


Figure 1. Schematic diagram of a thin layer electrode. A and B indicate surfaces of working electrodes exposed to solution.

In many of the derivations which follow, one must consider the nature of the charge transfer process. Thus introduced in this section are several fundamental equations for reversible and irreversible charge transfer processes. These equations are derived for a Faradaic process described by the chemical equation $O + ne \rightleftharpoons R$ with unity stoichiometric coefficients. Both O and R are assumed to be soluble. For a reversible system in which the forward and backward reactions occur at essentially the same rate, the concentrations of O and R at the working electrode are related to potential as described by the Nernst equation.

$$E = E^{\circ'} + \frac{RT}{nF} \ln \frac{c_O^e}{c_R^e} \quad (1)$$

Here $E^{\circ'}$ (i.e., the formal potential) is related to the standard potential and the activity coefficients of O and R as indicated in Eq. (2).

$$E^{\circ'} = E^{\circ} + \frac{RT}{nF} \ln \frac{\gamma_O}{\gamma_R} \quad (2)$$

For irreversible systems, the kinetics of the charge transfer process must be considered. One method for doing this is to use the Eyring equation.

$$I = nFAk^{\circ} \left\{ -c_O^e \exp \left[-\frac{\alpha n_a F}{RT} (E - E^{\circ'}) \right] + c_R^e \exp \left[\frac{(1 - \alpha) n_a F}{RT} (E - E^{\circ'}) \right] \right\} \quad (3)$$

This equation is valid even if $O + ne \rightleftharpoons R$ is a multistep process, provided that the rate is limited by a single sluggish step (i.e., the rate-determining step) and no adsorbed states are involved. In Eq. (3) double layer effects (i.e., the effect of the specific adsorption of ions or of diffuse layer voltage drops on the driving potential for a charge transfer reaction) are assumed to be insignificant.

For totally irreversible cases in which the back reaction can be neglected, Eq. (3) can be simplified to

$$I_c = -nFAk^{\circ} c_O^e \exp \left[-\frac{\alpha n_a F}{RT} (E - E^{\circ'}) \right] \quad (4)$$

for a cathodic reaction. Similarly, for an anodic reaction, one obtains

$$I_a = nFAk^{\circ} c_R^e \left[\frac{(1 - \alpha) n_a F}{RT} (E - E^{\circ'}) \right] \quad (5)$$

The equations given here are written with anodic currents positive and cathodic currents negative, to comply with IUPAC recommendations.

There are several factors (e.g., edge effects, solution resistance, and double layer capacitance) which can cause a thin layer system to not obey the equations derived in the following sections. When these factors are encountered one may want to modify the descriptive equations or the cell design.

2.1. Coulometry⁽⁹⁻¹¹⁾

In the most common coulometric experiment, potential step coulometry, the excitation is a potential step from E_1 , where essentially all the electroactive species is in one form (i.e., O or R), to E_2 , where the electroactive species is in the other form. The resulting current is integrated and recorded as a function of time as shown in Figure 2. (A related experiment, potential scan coulometry, is discussed in Reference 12.)

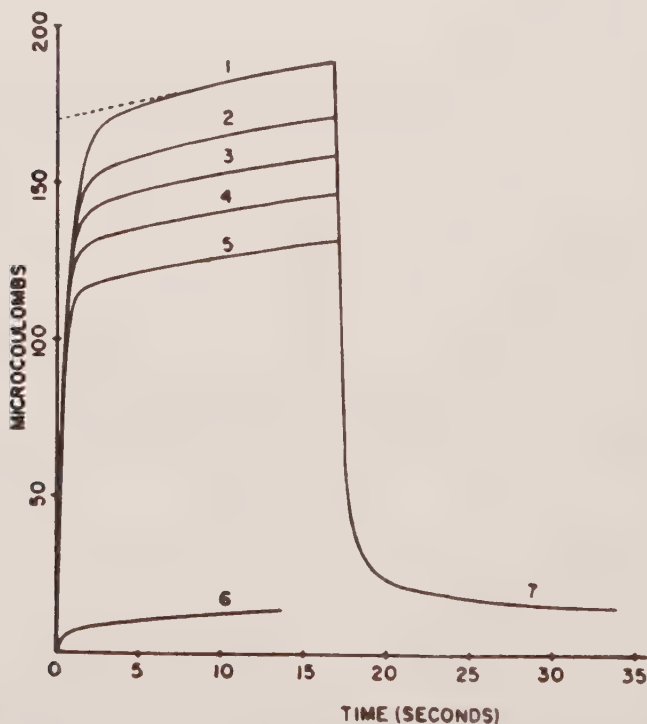


Figure 2. Q - t curves on a Hg-coated Pt electrode: $1.040 \times 10^{-3} M$ Cu^{+2} in $1 M$ NO_3^- , potential stepped from $+0.15$ to -0.20 volt and vice versa. Solution thickness: (1) 3.05×10^{-3} ; (2) 2.8×10^{-3} ; (3) 2.54×10^{-3} ; (4) 2.28×10^{-3} ; (5) 2.03×10^{-3} cm; (6) background curve on $1 M$ KNO_3 ; (7) stripping curve. [Reprinted with permission from D. M. Oglesby, S. H. Omang, and C. N. Reilley, *Anal. Chem.* **37**, 1312 (1965). Copyright 1965, American Chemical Society.]

The total charge (measured by extrapolating the plateau to $t = 0$) includes both faradaic and background (e.g., double layer charging, electrode or solvent electrolysis, etc.) components as indicated in Eqs. (6 and 7).

$$Q_c^T = -nFVc_O^0 + Q_b \quad (6)$$

$$Q_a^T = nFVc_R^0 + Q_b \quad (7)$$

The background charge, Q_b , is usually evaluated by performing the experiment in the absence of reactant; however, in instances where the background contribution is not independent of the presence of reactant, this method yields invalid results. While the charge transfer rate does affect the time required to reach the plateau, it does not govern the height of the plateau. Thus Eqs. (6 and 7) are valid for both reversible and irreversible systems. In addition, since no diffusion coefficients appear in these equations, Q_c^T and Q_a^T are essentially independent of temperature, ionic strength, and viscosity.

2.2. Chronopotentiometry^(3,13-15)

In a thin layer chronopotentiometry experiment, the potential required to maintain a constant anodic or cathodic current between the working and auxiliary electrodes is recorded as a function of time. For example, to maintain a constant cathodic current through a solution of some oxidized species requires increasingly negative potentials to compensate for the depletion of that species (see Figure 3). Thus under ideal conditions, after the oxidized species is completely reduced (i.e., after transition time τ), a rapid negative increase in the applied potential is observed.

The rate of charge transfer can affect chronopotentiometric results. If a system behaves irreversibly, more negative potentials are required to maintain a given cathodic current than would be required for a reversible system under identical conditions. The increased potentials are necessary to compensate for

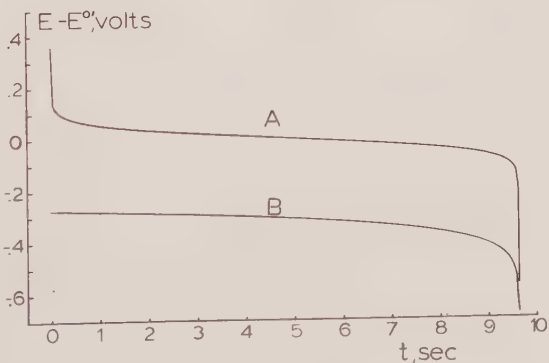


Figure 3. Theoretical thin layer chronopotentiometric potential-time curves for a cathodic current. (A) Reversible reduction; (B) Irreversible reduction ($k^\circ = 10^{-6} \text{ cm sec}^{-1}$). Values of the parameters assumed in making the plots were $A = 0.5 \text{ cm}^2$, $\alpha = 0.5$, $c_O^0 = 10^{-3} \text{ mole cm}^{-3}$, $I_c = -10 \text{ } \mu\text{A}$, $n = 1$, $n_a = 1$, $T = 298 \text{ K}$, and $V = 10^{-3} \text{ cm}^3$.

the sluggishness of the charge transfer process. This is demonstrated by curves *A* and *B* in Figure 3.

The total transition time, τ , is independent of diffusional processes, provided $\tau \geq \ell^2/3D\epsilon$ where ϵ is the relative error in c^0 if calculated from Eqs. (8 or 9), and D is the diffusion coefficient of the species reacting at the electrode.⁽⁶⁾ This equation indicates that to ensure thin layer conditions, the electroactive species must be close to the electrode (i.e., ℓ small enough) and not forced to undergo charge transfer at too rapid a pace (i.e., τ long enough). If these requirements are met, the equations for transition times are

$$\tau_c = -\frac{nFVc_O^0}{I_c} + \frac{Q_b}{I_c} \quad (8)$$

$$\tau_a = \frac{nFVc_R^0}{I_a} + \frac{Q_b}{I_a} \quad (9)$$

Here, Q_b represents the charge due to background processes which occur during the transition time. If the background processes are reversible, then Q_b can be evaluated by measuring Q for a blank solution as the applied potential is varied from E_{initial} to E_{final} . (These potentials refer to the initial and final potentials measured at $t = 0$ and $t = \tau$ in the original chronopotentiometric experiment with reactant present.) Unfortunately, if the background processes are irreversible, evaluating Q_b is more difficult since Q_b now depends not only on the initial and final potentials, but also on how the potential varies with time in the original experiment.

Assuming thin layer conditions hold, the equations relating potential and time are derived by combining Faraday's law (in a time-dependent form as shown in Eqs. (14 and 15) and the appropriate charge transfer equation (Eqs. 1-5). For a reversible system with a cathodic current, the result is

$$E = E^{o'} + \frac{RT}{nF} \ln \left[-\frac{nFVc_O^0}{I_c t} - 1 \right] \quad (10)$$

and for an anodic current

$$E = E^{o'} - \frac{RT}{nF} \ln \left[\frac{nFVc_R^0}{I_a t} - 1 \right] \quad (11)$$

On the other hand, for a totally irreversible system with a cathodic current, the equation is

$$E = E^{o'} + \frac{RT}{\alpha n_a F} \ln \left[-\frac{nFAk^o}{I_c} \left(c_O^0 + \frac{I_c t}{nFV} \right) \right] \quad (12)$$

and for the anodic current

$$E = E^{o'} - \frac{RT}{(1 - \alpha) n_a F} \ln \left[\frac{nFAk^o}{I_a} \left(c_R^0 - \frac{I_a t}{nFV} \right) \right] \quad (13)$$

Eqs. (10 and 12) are plotted in Figure 3.

Chronopotentiometry has fallen out of favor due to the fact that τ is often hard to determine (due to background reactions, ohmic polarization, or edge effects) and that evaluating Q_b can be troublesome.

2.3. Cyclic Voltammetry^(16,17)

In cyclic voltammetry, where current is measured as a function of a linearly varying applied potential, the descriptive equations are comparatively simple, provided thin layer conditions persist (i.e., the solution thickness is thin enough and the sweep rate is slow enough that the concentrations of O and R remain homogeneous while the potential is scanned). Equations describing the thin layer requirements are given in Reference 6.

Neglecting background currents, Faradaic current is directly related to the rate of change in the concentration of the reactant as given by the differential form of Faraday's law.

$$I_c = nFV \frac{dc_O}{dt} \quad (14)$$

$$I_a = -nFV \frac{dc_R}{dt} \quad (15)$$

The time dependence of the applied potential can be written as

$$E = rt + E_{t=0} \quad (16)$$

where $r = dE/dt$ and $E_{t=0}$ is the applied potential at the beginning of the scan. By combining Eqs. (14) or (15) with Eq. (16) and the appropriate charge transfer equation (see Eqs. 1-5), expressions relating Faradaic current and applied potential can be derived. For a reversible system in which both O and R are soluble, the results obtained for an anodic or cathodic scan are

$$I = \frac{n^2 F^2 r V c_T \theta}{RT(1 + \theta)^2} \quad (17)$$

$$E_p = E^{\circ'} \quad (18)$$

$$I_p = \frac{n^2 F^2 r V c_T}{4RT} \quad (19)$$

where $\theta = \exp[(nF/RT)(E - E^{\circ'})]$. Though perhaps not readily apparent from Eqs. (17 and 19), the anodic and cathodic currents described by these equations are of opposite sign. This is due to the fact that during an anodic scan r is positive, but during a cathodic scan r is negative. For cathodic currents in a totally irreversible system (i.e., the peak current is more than one hundred

times larger than the exchange current) the following equations apply:

$$I_c = -nFAk^\circ c_T \exp \left\{ -\frac{\alpha n_a F}{RT} (E - E^{\circ'}) + \frac{ARTk^\circ}{\alpha n_a FVr} \exp \left[-\frac{\alpha n_a F}{RT} (E - E^{\circ'}) \right] \right\} \quad (20)$$

$$E_{c,p} = E^{\circ'} + \frac{RT}{\alpha n_a F} \ln \left[-\frac{ARTk^\circ}{\alpha n_a FVr} \right] \quad (21)$$

$$I_{c,p} = \frac{\alpha n_a n F^2 V r c_T}{eRT} \quad (22)$$

The corresponding equations for an anodic current are

$$I_a = nFAk^\circ c_T \exp \left\{ \frac{(1-\alpha)n_a F}{RT} (E - E^{\circ'}) - \frac{ARTk^\circ}{(1-\alpha)n_a FVr} \exp \left[\frac{(1-\alpha)n_a F}{RT} (E - E^{\circ'}) \right] \right\} \quad (23)$$

$$E_{a,p} = E^{\circ'} - \frac{RT}{(1-\alpha)n_a F} \ln \left[\frac{ARTk^\circ}{(1-\alpha)n_a FVr} \right] \quad (24)$$

$$I_{a,p} = \frac{(1-\alpha)n_a n F^2 V r c_T}{eRT} \quad (25)$$

More detailed derivations of Eqs. (17-25), with corrections for potential drops across the diffuse double layer, and equations for semi-reversible charge transfer systems are given in Reference 16.

As might be expected from the preceding equations, a cyclic voltammogram reflects the properties of the charge transfer process being observed. Theoretical voltammograms are plotted in Figure 4 using various values for k° . While for reversible systems the anodic and cathodic peak currents occur at the same potential, as the charge transfer process becomes slower (i.e., k°

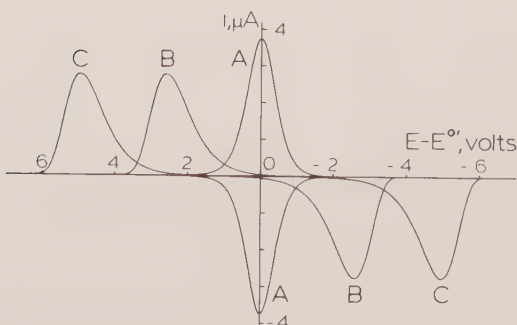


Figure 4. Theoretical cyclic current-potential curves in thin layers of solution for various values of k° . (A) Reversible reaction; (B,C) Totally irreversible reactions; k° : (B) 10^{-6} , (C) 10^{-8} cm sec $^{-1}$. The following values were assumed in making the plots: $\alpha = 0.5$, $V = 2 \times 10^{-3}$ cm ^{3} , $|r| = 2 \times 10^{-3}$ V sec $^{-1}$, $n = 1$, $n_a = 1$, $A = 0.5$ cm ^{2} , $c_T = 10^{-6}$ mole cm $^{-3}$, $T = 298$ K.

decreases) the current peaks are shifted apart with only modest changes in the shape. Unlike k° , α has a strong influence on the shape of the current peaks. As shown in Figure 5, decreasing α tends to broaden cathodic peaks and sharpen anodic peaks.

Thin layer cyclic voltammetry is in some instances more satisfactory than the same experiment in conventional cells. One reason for this is that since thin layer currents are usually more than an order of magnitude smaller, electrochemical systems behave more reversibly. In some cases this permits the study of reactions that are hidden under background reactions in conventional cells.⁽¹⁷⁾ Two other advantages are that multiple sweeps do not alter the basic equations and that a sweep may be interrupted without affecting the experiment.

2.4. Steady-state Voltammetry^(8,18,19)

Four-electrode steady-state voltammetry requires two independently potentiostated working electrodes (on opposite sides of the thin layer) with provisions for monitoring the current through each. Reference and auxiliary electrodes are used in their usual configuration. Typical electronic circuitry for this experiment is given in Reference 18.

Before discussing the details of the steady-state voltammetry experiment, the nature and origin of the associated steady-state currents will be reviewed. If the two working electrodes are held at potentials such that O is generated at one electrode (anode) and R is generated at the other (cathode), and if the total concentration of O plus R remains constant, then eventually the concentrations of O and R must adjust so that the rates of production of O and R are equal. This is obvious since each reaction depends on the other for reactant and since no reaction can continuously consume more reactant than is being provided. Neglecting background reactions, since the electrochemical reactions of O and R are responsible for the working electrode currents, once equilibrium is achieved, these currents should be equal and remain constant (i.e., they are steady-state currents). Therefore, at steady state the fluxes of

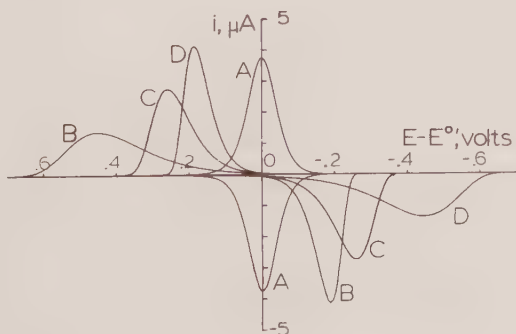


Figure 5. Theoretical cyclic current-potential curves in thin layers of solution for various values of α . (A) Reversible reaction; (B-D) Irreversible reactions, α : (B) 0.75, (C) 0.50, (D) 0.25. The following values were assumed in making the plots: $k^\circ = 10^{-6} \text{ cm sec}^{-1}$ (except Curve A); V , $|r|$, n , n_a , A , c_T and T as in Figure 4.

reactant to each of the working electrodes are equal. That is

$$\left(\frac{\partial c_O}{\partial x}\right)_c D_O = -\left(\frac{\partial c_R}{\partial x}\right)_a D_R \quad (26)$$

where $(\partial c_O/\partial x)_c$ refers to the concentration gradient of O at the cathode and x equals the distance from the cathode.

In the steady-state voltammetry experiment, one working electrode is held at a potential which is sufficiently far from $E^{\circ'}$ to ensure the presence of only O or only R , while the potential of the other electrode is scanned. The steady state current flowing through the electrode least susceptible to background currents is recorded as a function of the sweep potential. A typical steady-state voltammogram (cathodic scan) with the corresponding concentration profiles for several points on the curve is given in Figure 6.

As shown in Figure 6, at steady state the O and R concentration profiles are linear. The justification for this is as follows. Since at steady state each of the electroactive species is consumed and produced at the same rate, the concentrations of O and R remain constant at all points within the thin layer.

$$\frac{\partial c_O}{\partial t} = \frac{\partial c_R}{\partial t} = 0 \quad (27)$$

From Eq. (27) and Fick's second law, one obtains

$$\frac{\partial c_O}{\partial t} = D_O \left(\frac{\partial^2 c_O}{\partial x^2} \right) = 0 \quad (28)$$

which on integration gives

$$\frac{\partial c_O}{\partial x} = \text{constant} \quad (29)$$

Thus the concentration profile for species O must be linear. Species R can be treated similarly.

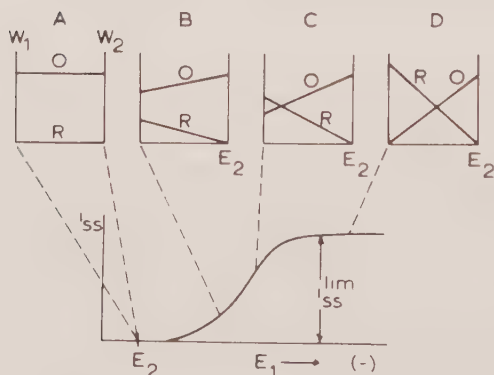


Figure 6. Steady-state current as a function of potential: (A) potential of both electrodes much more positive than the formal potential of the O/R couple; (B) potential of the cathode slightly less negative than $E^{\circ'}$; (C) potential of the cathode slightly more negative than $E^{\circ'}$; (D) potential of the cathode much more negative than $E^{\circ'}$. [From L. B. Anderson and C. N. Reilley, *J. Electroanal. Chem.* **10**, 295 (1965), with permission.]

Linear concentration profiles permit one to write several simple equations describing various aspects of a thin layer system under steady state conditions. First, the equal flux equation [i.e., Eq. (26)] can be simplified to

$$D_O(c_O^a - c_O^c) = D_R(c_R^c - c_R^a) \quad (30)$$

where c_O^a is the concentration of species O at the anode. Second, a simple equation can be written relating the O and R concentrations in the vicinity of the electrodes, to the total concentration of electroactive species

$$\frac{c_O^a + c_O^c}{2} + \frac{c_R^a + c_R^c}{2} = c_T \quad (31)$$

Finally, when used in conjunction with Fick's first law, linear concentration profiles yield uncomplicated expressions for steady-state currents.

$$I_{a,ss} = -I_{c,ss} = nF\mathcal{A}D_O\left(\frac{c_O^a - c_O^c}{\ell}\right) = nF\mathcal{A}D_R\left(\frac{c_R^c - c_R^a}{\ell}\right) \quad (32)$$

Here $\mathcal{A}$ refers to the cross-sectional area of the electrode cavity or the area of one of the working electrodes, not the total area of both working electrodes.

Frequently additional simplifications can be made to Eqs. (30)–(32); for example, when obtaining a cathodic steady-state voltammogram (see Figure 6), the anode is held at a potential such that $c_R^a = 0$. Moreover, in the case of a limiting steady-state current, as depicted in part D of Figure 6, both c_R^a and c_O^c equal zero.

The currents obtained in steady-state voltammograms depend on (among other things) the rates of diffusion of O and R , the potential at the scanning electrode, and the rate of charge transfer at that electrode. The charge transfer rate at the other working electrode is rendered unimportant by holding it at a potential sufficiently far from E° . Using the Eyring equation [i.e., Eq. (3)] written for the scanning electrode, the equal flux equation [i.e., Eq. (30)], and Eqs. (31) and (32), which provide useful expressions for the electrode concentrations contained in the Eyring equation, one can obtain an expression relating the steady-state current to the potential of the scanning electrode. For an anodic scan, the appropriate equation is

$$\frac{1}{\theta_1^{\alpha-1} k^\circ \ell} + \frac{\theta_1}{D_O} = \left(\frac{I_{a,ss}^{\text{lim}} - I_{a,ss}}{I_{a,ss}} \right) \left(\frac{D_O + D_R}{2D_OD_R} \right) \quad (33)$$

where $\theta_1 = \exp [(-n_a F/RT)(E - E^\circ)]$. Similarly, for a cathodic scan

$$\frac{1}{\theta_1^\alpha k^\circ \ell} + \frac{1}{D_R \theta_1} = \left(\frac{I_{c,ss}^{\text{lim}} - I_{c,ss}}{I_{c,ss}} \right) \left(\frac{D_O + D_R}{2D_OD_R} \right) \quad (34)$$

In the derivation of Eqs. (33) and (34), the complete Eyring equation is employed, thus the equations apply equally well to systems which exhibit semireversible or totally irreversible charge transfer kinetics. For reversible

systems, the k° containing terms in Eqs. (33) and (34) go to zero and the n_a in θ_1 becomes n . Additional details of the derivation of these equations are given in Reference 18.

The limiting currents ($I_{a,ss}^{\text{lim}}$ and $I_{c,ss}^{\text{lim}}$) referred to in Eqs. (33) and (34) are those currents obtained when the potentials at the two working electrodes are such that essentially only O exists at the anode and only R exists at the cathode. Using Eqs. (30)–(32) and setting c_O^c and c_R^a equal to zero, one can obtain

$$I_{c,ss}^{\text{lim}} = -\frac{2nFAc_T}{\ell} \left(\frac{D_O D_R}{D_O + D_R} \right) \quad (35)$$

The equation for an anodic limiting current is identical except in sign.

Steady-state voltammetry stands apart from the methods discussed previously in that even when thin layer conditions hold, diffusion of electroactive species must be considered. Moreover, the thickness of the layer affects the time required to reach a steady-state current. The descriptive equations may be found in References 6 and 8.

2.5. Diffuse Layer Treatment

In a recent publication by Farina and Oldham,⁽²⁰⁾ a treatment for the electric double layer in thin layer cells is presented. They point out that in thin layer cells of low ionic strength one must be concerned with the possibility of overlap of the diffuse layers from the two facing working electrodes. Thus the semi-infinite treatment used in Gouy–Chapman theory can be (in some cases) inadequate for describing thin layer systems.

2.6. Definition of Symbols

A	total geometric area of working electrode(s), cm^2
$\mathcal{A}$	cross-sectional area of electrode cavity, cm^2
α	charge transfer coefficient
c_O, c_R	concentration of O and R in the thin layer cavity, mol/cm^3
$c_O^a, c_R^a, c_O^c, c_R^c$	concentration of O and R at the anode or cathode (four-electrode configuration), mol/cm^3
c_O^e, c_R^e	concentration of O and R at the working electrode(s), mol/cm^3
c_O^0, c_R^0	initial concentration of O and R , mol/cm^3
c_T	total concentration of electroactive species (i.e., $c_O + c_R$), mol/cm^3
D_O, D_R	diffusion coefficient of O and R , cm^2/s
E	potential at working electrode relative to reference electrode, V
E°	standard potential, V
$E^{\circ'}$	formal potential, V

$E_{p,a}, E_{p,c}$	potential corresponding to a cyclic voltammetry current peak during an anodic or cathodic scan, V
e	2.718
ϵ	relative error (i.e., $\Delta x/x$)
F	Faraday constant, 9.64846×10^4 C/equivalent
γ_O, γ_R	molal activity coefficients for O and R
Γ_O, Γ_R	interfacial excess of O or R , mol/cm ²
I	current, A
I_a, I_c	anodic or cathodic current, A
$I_{p,a}, I_{p,c}$	peak current during an anodic or cathodic potential scan (cyclic voltammetry), A
$I_{a,ss}, I_{c,ss}$	anodic or cathodic steady-state current (steady-state voltammetry), A
$I_{a,ss}^{lim}, I_{c,ss}^{lim}$	limiting anodic or cathodic steady-state current (steady-state voltammetry), A
k°	standard charge transfer rate constant, cm/s
ℓ	thickness of thin layer of solution (i.e., separation between plane parallel working electrodes), cm
n	number of electrons transferred at the electrode per reactant molecule
n_a	number of electrons transferred up to and including the rate-determining charge transfer step
Q_a, Q_c	charge due to anodic or cathodic current, C
Q_a^T, Q_c^T	total charge due to anodic or cathodic currents, C
Q_b	charge due to background processes, C
T	temperature, °K
t	time, s
τ	transition time (chronopotentiometry), s
r	sweep rate (dE/dt), sign depends on whether scanning anodically or cathodically, V/s
R	ideal gas constant, 8.31551 J/(mol °K)
V	volume of thin layer cavity, cm ³
x	distance from cathode (steady-state voltammetry), cm

3. Thin Layer Cells

3.1. Cell Design Considerations

Two cell design problems which have continually plagued thin layer electrochemists are ohmic polarization and edge effects. Unfortunately, these two problems are interlinked in that correction for one has frequently resulted in magnification of the other. Since both problems are recurring themes in the history of thin layer cell development, they will be discussed prior to a survey of reported cell designs.

3.1.1. Ohmic Polarization

The solution resistance between the reference electrode and a particular point on the working electrode may be separated into two components: a constant component, R_u , and a component, R_x , which varies from point to point on the working electrode. R_u refers to the resistance between the reference electrode and its point of electrical contact with the thin layer of solution (e.g., a luggin capillary). This component of solution resistance is very similar to the uncompensated resistance in conventional cells. On the other hand, R_x is the resistance from the point of electrical contact to some point x on the working electrode. This R_x component is the factor responsible for ohmic polarization. Obviously there are many different values for R_x depending on what point on the working electrode is referred to, with points more distant from the point of contact experiencing larger resistances.

Voltage drops which occur across R_x are especially significant due to the relatively high resistance of the thin layer of solution and due to the fact that the reference and auxiliary electrode currents frequently share the same path through the thin layer. As a result of the various iR_x drops, it is virtually impossible to control or monitor the potential at all points on the working electrode simultaneously.

The effect of ohmic polarization depends on the nature of the experiment being performed. Perhaps the most obvious evidence of ohmic polarization occurs while electrochemically generating a colored product in an optically transparent thin layer electrode (O.T.T.L.E.).⁽²¹⁾ The colored product front is observed to move away from the edge of the cell nearest the reference and auxiliary electrodes.

The effect of ohmic polarization on cyclic voltammetry, chronopotentiometry, and potential step coulometry was investigated by Tom and Hubbard.⁽²²⁾ In their work, they compared the results obtained from an electrode in the conventional configuration and in the porous-boundary configuration. (The porous-boundary configuration practically eliminates ohmic polarization effects.) Their results for the Fe(III)–Fe(II) couple are given in Figures 7, 8, and 9. As indicated in the diagrams, ohmic polarization can cause experimental results to appear more charge transfer irreversible.

Goldberg and Bard have studied ohmic polarization in thin layer cells using digital simulation techniques.⁽²³⁾ They divided the thin layer of solution into homogeneous blocks and assumed all points within a given block experienced the same solution resistance to the reference electrode. Their theoretical results for the effect of ohmic polarization on chronopotentiometry and potential step coulometry showed the same trends as those obtained experimentally by Tom and Hubbard.⁽²²⁾

The effects of ohmic polarization in conventional thin layer electrodes can be minimized by careful adjustment of experimental parameters. First, the solution resistance should be minimized. This can be accomplished by

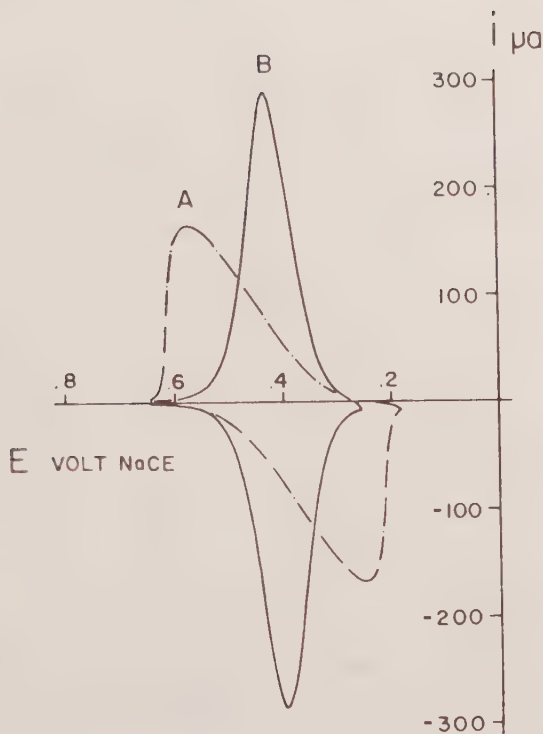


Figure 7. Cyclic current-potential curve for Fe(III)-Fe(II) at conventional and porous-boundary thin layer electrodes: (A) conventional micrometer electrode configuration; (B) porous-boundary micrometer electrode configuration. [Reprinted with permission from G. W. Tom and A. T. Hubbard, *Anal. Chem.* **43**, 671 (1971). Copyright 1971, American Chemical Society.]

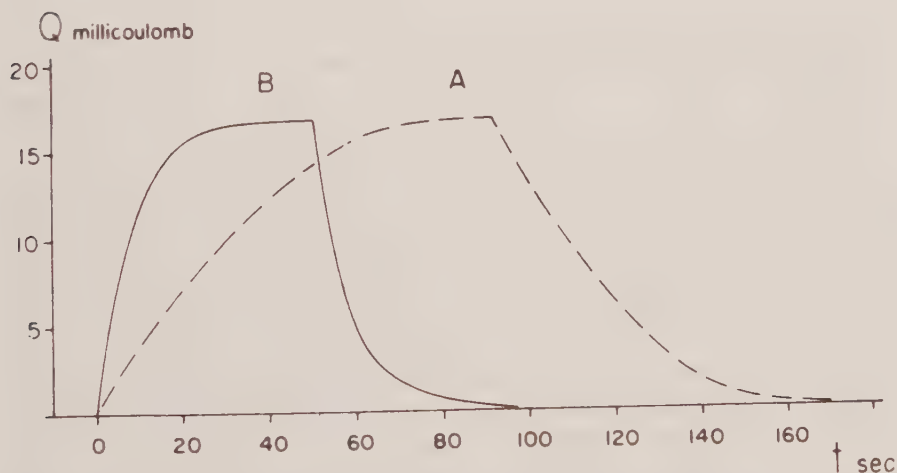


Figure 8. Potential-step coulometric curve for Fe(III)-Fe(II) at conventional and porous-boundary thin layer electrodes: (A) conventional micrometer electrode configuration; (B) porous-boundary micrometer electrode configuration. [Reprinted with permission from G. W. Tom and A. T. Hubbard, *Anal. Chem.* **43**, 671 (1971). Copyright 1971, American Chemical Society.]

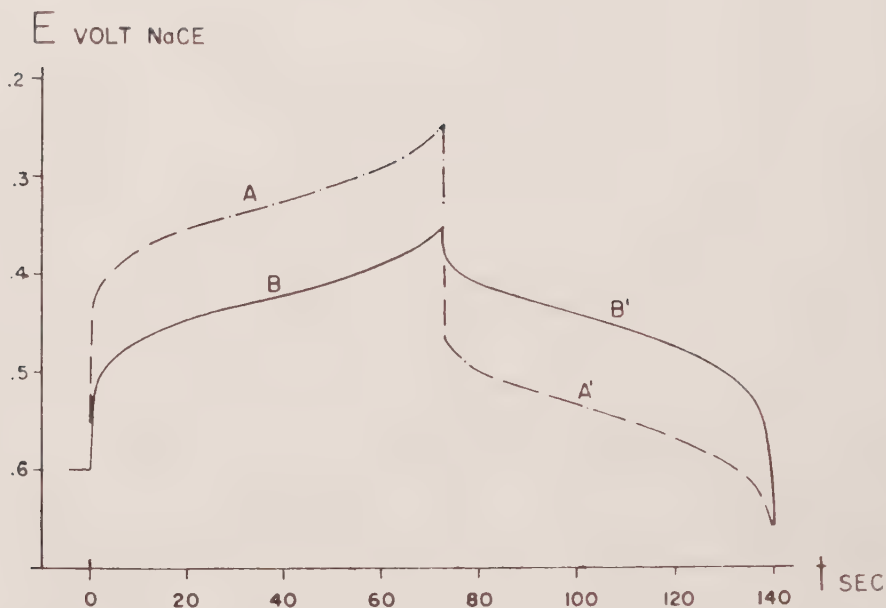


Figure 9. Chronopotentiometric curve for Fe(III)-Fe(II) at conventional and porous-boundary thin layer electrodes: (A) conventional micrometer electrode configuration; (B) porous-boundary micrometer electrode configuration. [Reprinted with permission from G. W. Tom and A. T. Hubbard, *Anal. Chem.* **43**, 671 (1971). Copyright 1971, American Chemical Society.]

using a strong concentration of supporting electrolyte (e.g., 1 F), by keeping the thin layer of solution as thick as possible, and by minimizing the separation between the point of electrical contact and the farthest point on the working electrode. Second, the current flowing through the cell needs to be kept small. This requires that the concentration of the reactant be low (e.g., $10^{-3} F$) and that the cell excitation be chosen so that large currents are not developed. Unfortunately, selecting optimum experimental parameters is actually more complicated than indicated above, since edge effects must also be considered.

Certain nonconventional cell designs are affected very little by ohmic polarization. Cell configurations in which the main current path is orthogonal to the current path to the reference electrode exhibit little ohmic polarization. This is due to the fact that the reference electrode does not experience the voltage drops caused by the main current. This condition has been realized in certain porous-boundary electrodes⁽²²⁾ and in four electrode systems at conditions of steady-state current.⁽¹⁹⁾ In addition, two electrode systems using an internal reference encounter essentially no polarization. Since the only solution resistance in these cells is that along a perpendicular path between two parallel electrodes, the voltage drop across the solution is approximately equal at all points on the working electrode.⁽²⁴⁾

3.1.2. Edge Effects

Edge effects refer to the diffusion of electroactive species into or out of the thin layer of solution via the edges of the thin layer cell. This effect is especially prevalent in cells where a significant portion of the thin layer edge is in contact with a large quantity of the reactant solution. Edge effects are readily apparent in potential step coulometry. As shown in Figure 2, edge effects can lead to a finite slope for the plateau region of $Q-t$ curves due to the influx of reactant into the thin layer cavity.

A primary advantage of doing electrochemistry in thin layer cells is that frequently diffusion processes can be ignored. Since to account for edge effects, diffusion must be considered, the minimization of edge effects has been a critical goal in cell design consideration. One approach taken to eliminate this problem is to isolate the solution in the thin layer cavity. For example, the thin layer of solution can be connected to the auxiliary and reference electrodes through a luggin capillary located at the perimeter of the thin layer (see Figure 1). However, while this method effectively controls edge effects, ohmic polarization often becomes bothersome. In sandwich-type cells (see Sections 3.2.2.1 and 3.2.2.2) edge effects can be particularly severe since one edge of the cell usually sits in a bulk solution of the electroactive species. One method for circumventing the edge effect problem in these cells is to have the area of solution exposed to the working electrode much larger than the area exposed to the bulk solution. (Unfortunately, this is in opposition to the requirements for minimization of ohmic polarization.) Another remedy to the edge effect problem in sandwich-type cells has been the installation of getter electrodes along the boundaries of the working electrode exposed to the bulk solution.⁽¹³⁾ The getter electrodes, which are maintained at the same potential as the working electrode, act as scavengers of electroactive species and thus prevent lateral diffusion of additional reactant into the active thin layer region.

3.2. Types of Thin Layer Cells

A multitude of thin layer electrodes have been reported in the literature. These include cells for general use,^(11,19,22,25-32) for spectroelectrochemical applications,^(13,21,33-39) for use as flow-through detectors,⁽⁴⁰⁻⁴³⁾ and for converting solar energy into electrical energy.^(44,45)

3.2.1. Conventional Cells

3.2.1.1. Micrometer-Type Cells

Many thin layer electrodes employ a micrometer as a means of varying the separation between opposite faces of the two working electrodes (from 1×10^{-3} cm). However, before the micrometer can provide an accurate knowledge of the solution thickness, it is necessary to establish the micrometer

setting at which the thickness is zero. This can be obtained from the $Q = \phi$ intercept on a plot of Q^T (coulometry) vs. micrometer reading.⁽¹¹⁾

Hubbard and Anson⁽²⁵⁾ reported the first micrometer-type electrode (see Figure 10.) In their electrode the solution was confined to the cavity between two platinum working electrodes. Both electrodes were insulated from the body of the micrometer allowing independent control of each electrode. The thin layer of solution was connected to the reference and auxiliary electrodes through a contact arm leading to an H cell of the type shown in Figure 11. While edge effects for this electrode were insignificant (less than 2% after 60 minutes with a 0.1 *M* Fe(III) solution and a 3.6×10^{-3} cm gap), ohmic contributions to the electrode potentials became appreciable at currents larger than 25 μ A.

A micrometer-type electrode which reduced the ohmic polarization associated with the Anson and Hubbard cell was introduced by Oglesby, Omang, and Reilley.⁽¹¹⁾ In this cell the thin layer of solution was completely surrounded by bulk solution in a Teflon cup (see Figure 12). The relatively large cross-sectional area of the current path to the reference and auxiliary electrodes led to reduced ohmic polarization but increased edge effects. These workers also demonstrated that the useful cathodic range of the platinum electrode could be extended to approximately -1.3 volts vs. S.C.E. by coating it with mercury.

Hubbard and Anson⁽²⁶⁾ developed a complex, micrometer-based electrode which realized hydrogen overpotentials comparable to those attained on a dropping mercury electrode. This design, which employed a mercury pool as the working electrode, demonstrated a larger cathodic potential limit than that obtained with the mercury-coated platinum electrode.

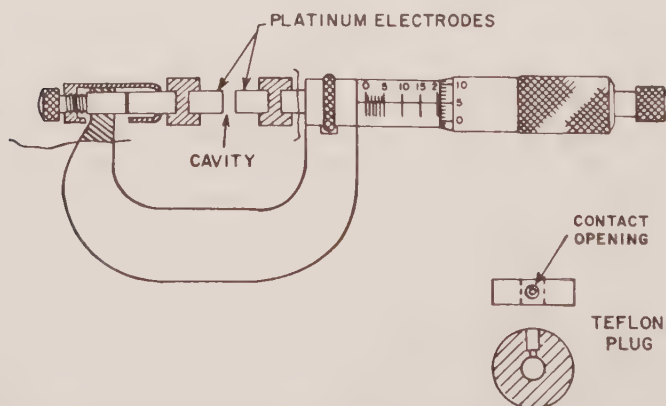


Figure 10. Micrometer electrode. The Teflon plug surrounds the thin layer of solution. [Reprinted with permission from A. T. Hubbard and F. C. Anson, *Anal. Chem.* **36**, 723 (1964). Copyright 1964, American Chemical Society.]

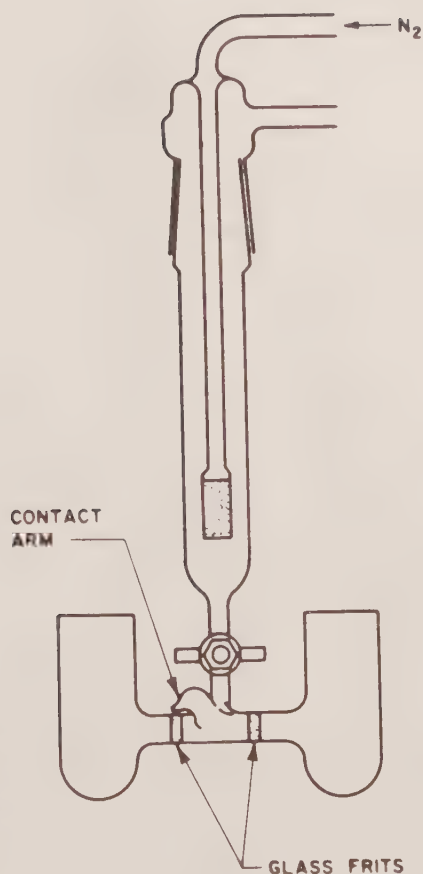


Figure 11. H cell for use with the micrometer electrode. One compartment contains the auxiliary electrode and the other compartment contains the reference electrode. [From A. T. Hubbard and F. C. Anson, in *Electroanalytical Chemistry*, A. J. Bard, ed., Vol. 4, p. 129, Marcel Dekker, New York (1971). Courtesy of Marcel Dekker, Inc.]

A dip-type electrode which also featured micrometer adjustment of solution thickness was reported by McClure and Maricle.⁽²⁷⁾ This electrode provided a convenient method for *in situ* n -value or concentration determinations.

A micrometer-type porous-boundary electrode (Figure 13) reported by Tom and Hubbard,⁽²²⁾ was shown to have substantially smaller iR drops and more uniform current densities than conventional designs. This was accomplished by providing perpendicular paths for the reference current (through the luggin capillary) and auxiliary current (through the porous boundary). The electrode shown in Figure 13 was designed to be used in both the conventional configuration (with both the reference and auxiliary electrodes connected via the luggin capillary) and in the porous-boundary configuration (with the auxiliary electrode behind the porous boundary). This allowed quick comparisons of the characteristics of the two configurations. Choice of the proper porous boundary was critical since diffusion of reactant through the

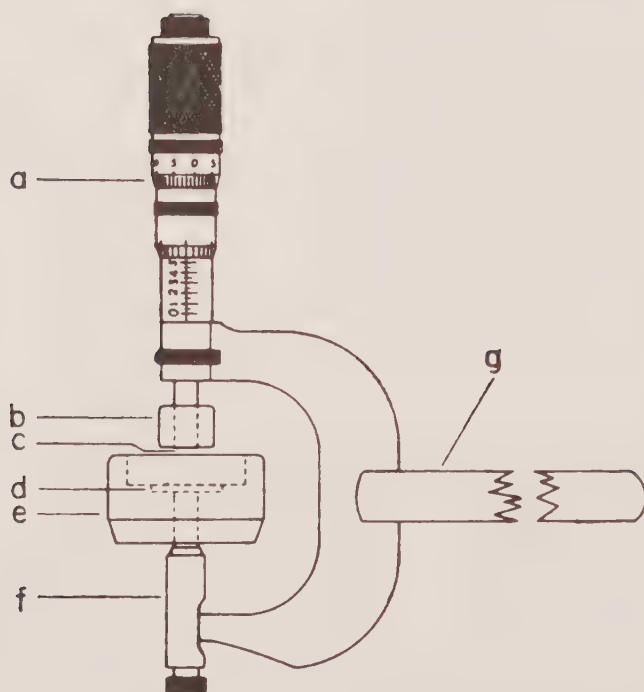


Figure 12. Thin layer micrometer electrode: (a) outer thimble for direct reading to one ten-thousandth of an inch; (b) press-fitted Teflon collar; (c) platinum face of the micrometer spindle; (d) flat glass disc pressed into the Teflon cup against the face of the detachable anvil; (e) cup machined from Teflon; (f) Starrett No. 212 detachable anvil; (g) stainless steel rod for mounting cell assembly. [Reprinted with permission from D. M. Oglesby, S. H. Omang, and C. N. Reilley, *Anal. Chem.* **37**, 1312 (1965). Copyright 1965, American Chemical Society.]

boundary was a potential problem. In this cell, Tom and Hubbard used for the porous boundary a platinum spinnerette disk (6.35 mm in diameter) which contained 21 evenly spaced holes, 0.02 mm in diameter.

Usually experimental parameters can be adjusted to diminish the effects of ohmic polarization; however, in solutions of poorly conducting electrolytes this may be impossible. In such cases the porous-boundary electrodes are especially advantageous.

3.2.1.2. Capillary-Wire Electrodes

Hubbard and co-workers have reported a number of capillary-wire type electrodes.^(6,8,22,25) A recent model is given in Figure 14.⁽⁶⁾ In this cell the thin layer of solution lies between a rod-shaped piece of electrode material and a section of precision bore, heavy wall, Pyrex[®] tubing. The electrode rod is flanged to insure uniform spacing of about 2×10^{-3} cm between the electrode rod and the glass wall. The electrode cavity is filled by capillary action and

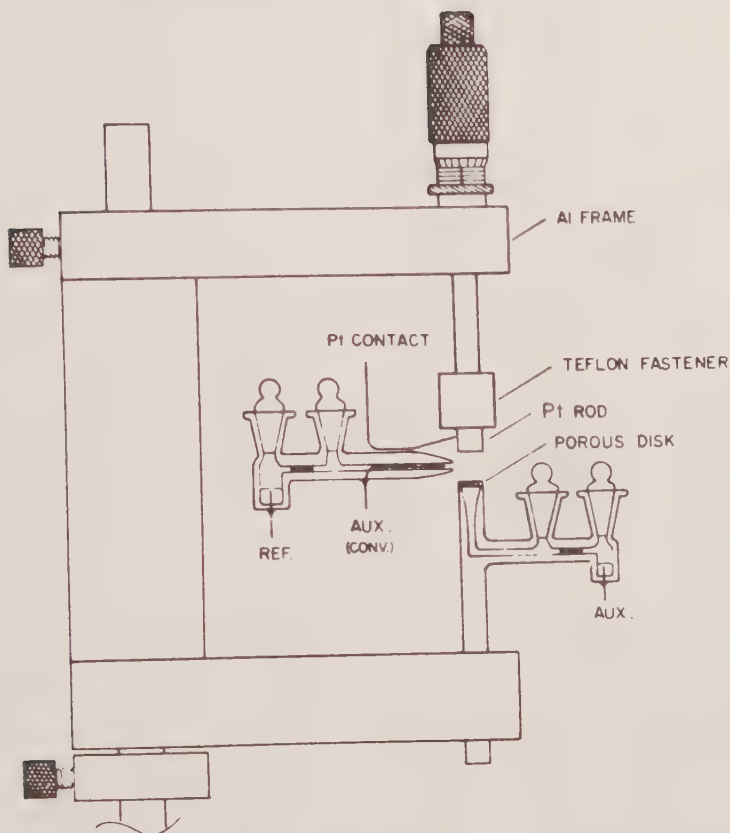


Figure 13. Micrometer porous-boundary thin layer electrode. [Reprinted with permission from G. W. Tom and A. T. Hubbard, *Anal. Chem.* **43**, 671 (1971). Copyright 1971, American Chemical Society.]

emptied by applying an inert gas under pressure. A similar cell has been constructed of fused quartz to study solutions in molten salts.⁽⁶⁾

A capillary-wire electrode (see Figure 15) incorporating a porous boundary (for minimization of ohmic polarization problems) has been reported.⁽²²⁾ This electrode employs a section of porous Vycor glass (rather than the precision bore Pyrex[®]) as the outer boundary of the thin layer. The auxiliary electrode current path is through the porous Vycor glass and perpendicular to the reference electrode current path which runs parallel to the electrode rod. (It has been noted⁽²⁸⁾ that porous glass boundaries can cause problems due to diffusion and adsorption of electroactive species in the porous glass.)

A cell similar to that discussed above, which allowed recovery and gas chromatograph analysis of electrolysis products, was reported by Hanley and Peters.⁽²⁹⁾

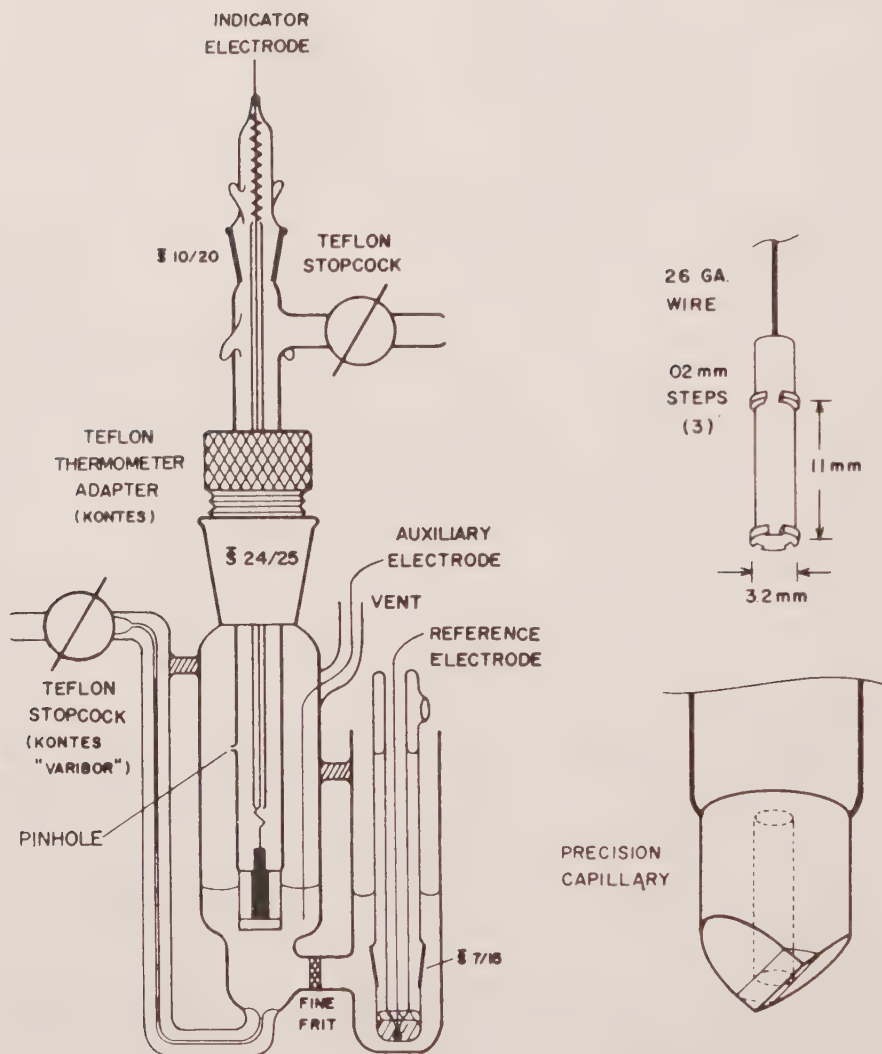


Figure 14. Capillary-wire thin layer electrode. [Reprinted with permission from A. T. Hubbard in *CRC Critical Reviews in Analytical Chemistry* 3, 201 (1973). Copyright The Chemical Rubber Co., CRC Press, Inc.]

Mark *et al.*^(28,30) have reported several thin layer cell designs which used a Nafion (DuPont) membrane to separate a platinum or gold wire working electrode from the supporting electrolyte solution containing the reference and auxiliary electrodes (Figure 16). Since the Nafion membrane is permeable to cations but impermeable to anions and large neutral species, some care was exercised when deciding what electrochemical systems were used in these cells.

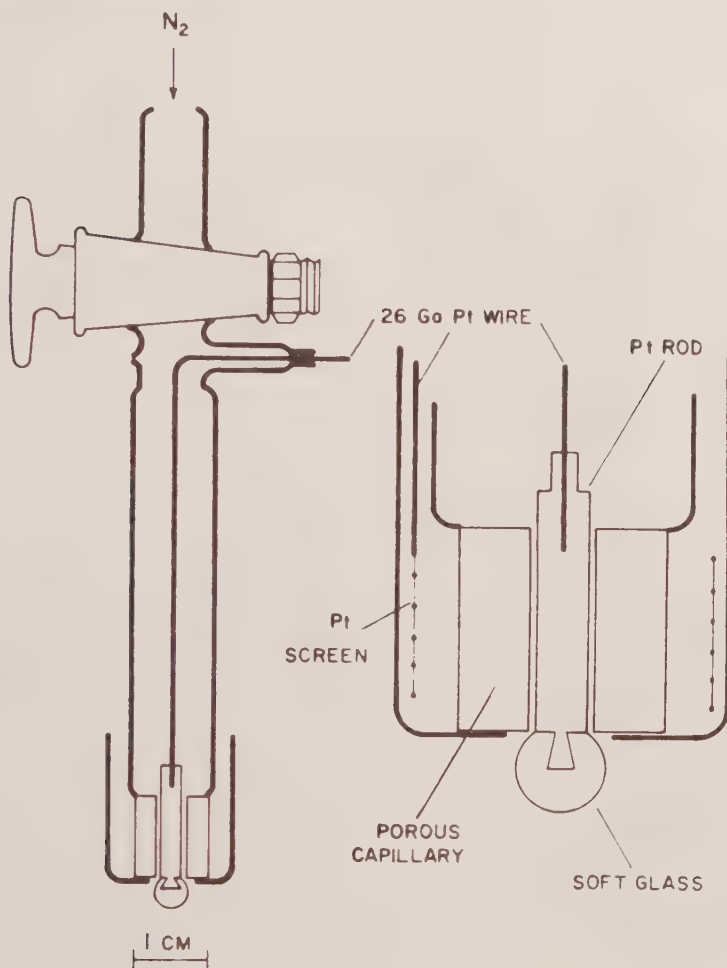


Figure 15. Capillary-wire porous-boundary thin layer electrode. The platinum screen which surrounds the porous capillary serves as the auxiliary electrode. [Reprinted with permission from G. W. Tom and A. T. Hubbard, *Anal. Chem.* **43**, 671 (1971). Copyright 1971, American Chemical Society.]

Several of the advantages given for the Nafion boundary cells were: minimization of ohmic polarization, low construction cost, ease of use, and an extremely small thin layer cavity. However, cyclic voltammograms at slow sweep rates (1 mV/s) indicated some departure from ideal thin layer behavior. This was assumed to be due to the finite resistance of the Nafion membrane and due to the fact that the reference electrode was located far from the working electrode.

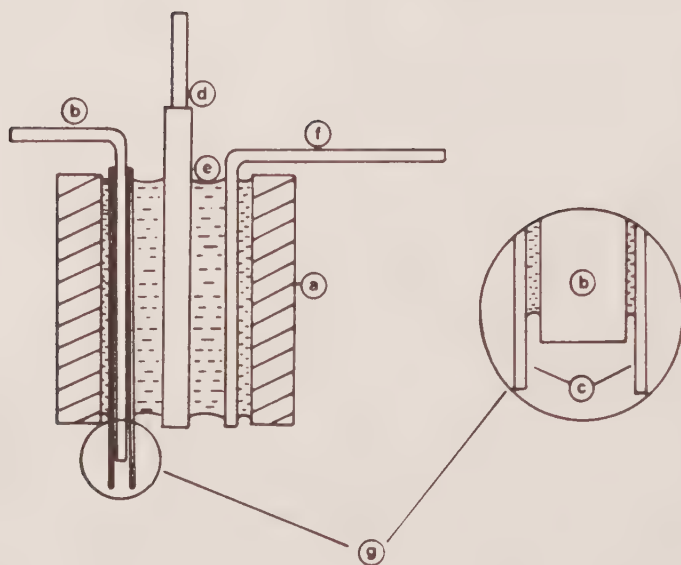


Figure 16. Thin layer cell. (a) Teflon tubing, i.d. 1.6 mm; (b) gold wire; (c) Nafion membrane; (d) reference electrode; (e) solution outside of thin layer electrode; (f) auxiliary electrode (gold wire); (g) expanded view of the tip of the thin layer electrode. [Reprinted with permission from J. Caja, A. Czerwinski, and H. B. Mark, Jr., *Anal. Chem.* **51**, 1328 (1979). Copyright 1979, American Chemical Society.]

3.2.1.3. Modified Spectrophotometer Cells

Two cells for general use have been reported which were constructed by modifying commercially available spectrophotometer cells. One involved modification of a Beckman type VT-02 variable geometry infrared cell.⁽³¹⁾ This cell used porous Vycor glass as one of the thin layer boundaries. The other cell was constructed from a Beckman type BT-10 variable pathway UV cell.⁽³²⁾

3.2.2. Spectroelectrochemical Cells

Thin layer electrodes are for the most part ideally suited for coupling with spectroscopic methods. Since a reactant can be exhaustively electrolyzed in a few seconds, interfering spectroscopic absorption of that reactant can be virtually eliminated. It is also possible to spectrally observe subsequent product reactions on time scales inconveniently slow for methods requiring diffusion of the reactant to the electrode.

The spectroscopic methods used in conjunction with thin layer electrodes are numerous and include UV-VIS,^(13,34,35,38) IR,^(13,33) fluorescence,⁽¹³⁾ specular reflectance,^(36,37) and laser Raman spectroscopy.⁽³⁹⁾ Also, the possibility of using thin layer electrodes in conjunction with electron spin resonance

methods has been suggested.^(1,13) A useful supplement to the discussion given here can be found in Heineman's review⁽⁴⁶⁾ of spectroelectrochemistry.

3.2.2.1. Minigrid Electrodes

The first optically transparent thin layer electrode (O.T.T.L.E.) was reported by Murray, Heineman, and O'Dom.⁽²¹⁾ Their cell, which was designed for operation in the UV-VIS region, consisted of a gold minigrid (1000 wires/inch with % $T = 45$) sandwiched between optically flat glass or quartz slides (see Figure 17). Teflon tape spacers were used to hold the slides together and to determine the breadth of the thin layer on either side of the minigrid electrode. As shown in Figure 17, the edges of the cell were sealed except at the bottom and at point A. By applying suction at point A, the thin layer cell was replenished from the reservoir in which it sat.

To compensate for the weaker intensities of infrared absorptions as compared to those at shorter wavelengths, Murray *et al.*⁽³³⁾ constructed a multilayer minigrid electrode. Four gold minigrids (100 wires/inch with 82% T) were used, resulting in an overall transmission of only 30% for the cell. This cell maintained the rapid response characteristics of single grid electrodes while providing a longer optical path for the infrared beam.

In an effort to improve the electrochemical characteristics of minigrid working electrodes, mercury films on a variety of substrates have been examined.^(34,47,48) For example, Heineman and co-workers⁽³⁴⁾ studied the hydrogen overvoltage shift obtained after a 200 Å mercury film was deposited on a nickel minigrid. While still short of that obtained on a hanging drop mercury electrode, the negative potential limit was extended to beyond -0.9 volts vs. S.C.E. for a 1 N HCl solution. Deposition of the small amounts of mercury required to achieve the extended cathodic range caused no measurable attenuation of the optical transparency of the nickel minigrid (i.e., 57% T with 333 wires/inch).

Heineman *et al.*⁽³⁵⁾ have modified a minigrid sandwich-type cell to permit removal of dissolved oxygen from the solution. The solution is degassed while in a degassing bulb by repetitive vacuum-nitrogen cycles. Then the solution is introduced into the thin layer cavity. This cell is unique in that a total solution volume of 500 μL is adequate.

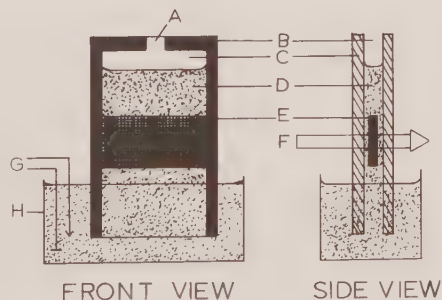


Figure 17. Optically transparent thin layer electrochemical cell (sandwich-type, not to scale). (A) Point of suction application to change solution; (B) Teflon tape spacers; (C) microscope slides; (D) solution; (E) transparent gold minigrid (working electrode); (F) optical path of spectrophotometer; (G) reference and auxiliary electrodes; (H) cup containing bulk solution.

3.2.2.2. Thin Film Electrodes

A sandwich-type cell which used a thermally evaporated, thin platinum (or gold) film as the working electrode was developed by Reilley and co-workers.⁽¹³⁾ The films had a resistance of about 10 ohms/cm at 20% transmittance. These thin film electrodes have been used for IR (sodium chloride substrate) and UV-VIS (quartz substrate) transmission experiments,⁽¹³⁾ for fluorescence spectroscopy,⁽¹³⁾ and for specular reflectance.⁽³⁶⁾ The configuration used for specular reflectance experiments is given in Figure 18. (This method is advantageous in that the light passes through the thin layer twice thereby increasing the optical sensitivity.) Shown in Figure 19 is the configuration used for simultaneous electrochemical-fluorescence studies. Using this technique solutions as dilute as $5 \times 10^{-6} M$ (aromatic hydrocarbons) have been studied.⁽¹³⁾

3.2.2.3. Long Optical Path Cells

One drawback to thin layer spectroelectrochemical cells is that the optical paths are usually short, resulting in decreased optical sensitivity. It has already been mentioned that increased optical sensitivity can be obtained by stacking several minigrid sandwich cells. Included in this section are two thin layer cells which employed completely different methods to increase the cells' optical sensitivity.

Aikens *et al.*⁽³⁷⁾ have constructed a thin layer cell for use in multiple specular reflectance spectroscopy. As shown in Figure 20, two facing gold mirrors served as working electrodes. Before leaving the cell, the laser excitation (632.8 nm) was reflected between the gold mirrors hundreds of times. This provided a drastic increase in the cell's optical sensitivity. Unfortunately, the authors had little success when attempting to replace the laser with a focused xenon lamp (presumably due to beam divergence within the cell).

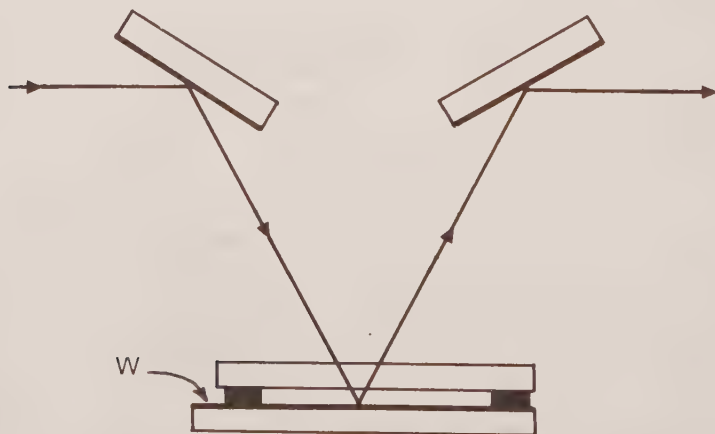


Figure 18. Basic configuration for specular reflectance in thin layer electrochemistry (top view). W = deposited metal film.

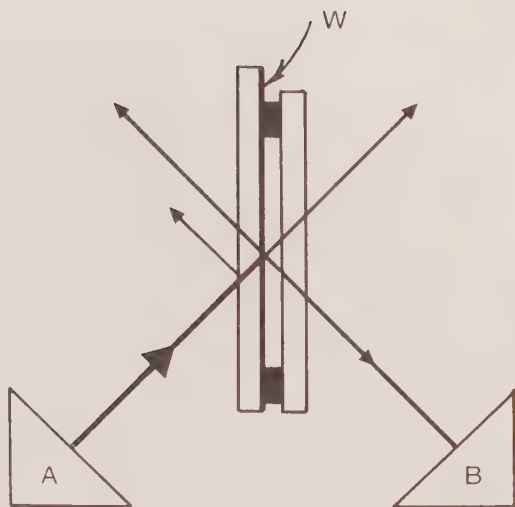


Figure 19. Fluorescence configuration (top view). (A) Source, (B) detector. W = deposited metal film.

J. L. Anderson⁽³⁸⁾ has designed what he calls a circulating, long-optical-path, spectroelectrochemical thin-layer (C.L.O.S.E.T.) cell. A long optical path is obtained by attaching an optical chamber (1 cm long by ca. 3 mm $\times$ ca. 7 mm; volume ca. 200 μ l) to the side of a thin layer cavity (volume ca. 350 μ l). The remote optical path is coupled to the thin layer cavity by a magnetically driven circulating pump located in the thin layer cavity. Anderson claims that the cell is dramatically more optically sensitive than other (O.T.T.L.E.) cells, while still exhibiting rapid electrolysis. However, he points out that the cell is plagued by a large uncompensated resistance.

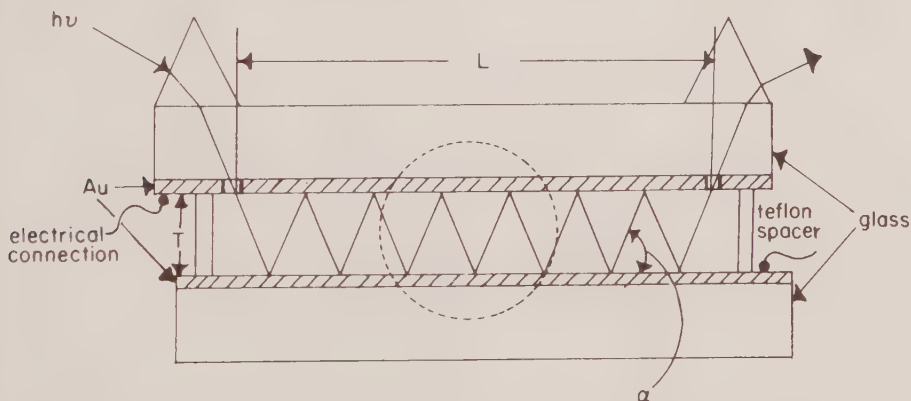


Figure 20. Cross section of the multiple specular reflection spectroelectrochemical cell. Not to scale. The dotted circle indicates the filling tube. [Reprinted with permission from C. E. Baumgartner, G. T. Marks, D. A. Aikens, and H. H. Richtol, *Anal. Chem.* **52**, 267 (1980). Copyright 1980, American Chemical Society.]

3.2.2.4. Laser Raman Cell

A serious hindrance to the coupling of electrochemistry and infrared spectroscopy has been that the principal electrochemical solvent, water, absorbs strongly in the infrared region. However, in Raman spectroscopy this limitation does not apply, since negligible absorption occurs when visible radiation is used as the exciting source, and since the symmetric bending vibration of water has a weak Raman intensity.

A micrometer-type cell for use in laser Raman spectroscopy was reported by Clarke *et al.*⁽³⁹⁾ (see Figure 21). The laser beam transverses the thin layer of solution in a path parallel to the platinum working electrode, while the scattered radiation was observed along a path orthogonal to the face of the working electrode.

3.2.3. Flow through Electrochemical Detectors

An extremely sensitive thin layer electrochemical detector for liquid chromatography has been reported by Kissinger *et al.*⁽⁴⁰⁾ The detector uses a carbowax working electrode located in the effluent of an LC column. A conventional three-electrode potentiostatic system is used with the reference and auxiliary electrodes located downstream from the detector in an overflow vessel. (In a more recent paper,⁽⁴¹⁾ it has been pointed out that a more favorable position for the auxiliary electrode is directly across the flow stream from the working electrode.) In addition to extraordinary sensitivity (50–100 picograms), the active volume of the detector is only about 0.7 μl .

Along a similar vein, a tubular platinum electrode, which allowed electrochemical analysis of material flowing through the electrode, was designed and studied by Blaedel *et al.*⁽⁴²⁾ This electrode exhibited both high sensitivity (detection at below $10^{-8} M$) and low solution holdup (2–10 μl).

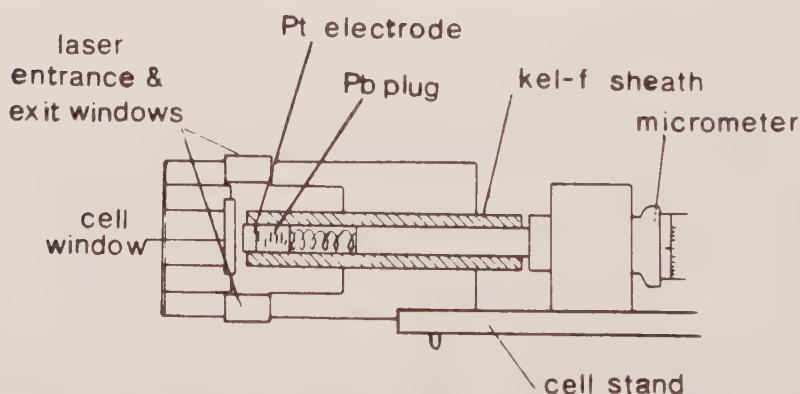


Figure 21. Sectional view of micrometer-type thin layer cell for use in laser Raman spectroscopy. [From J. S. Clarke, A. T. Kuhn, and W. J. Orville-Thomas, *J. Electroanal. Chem.* **54**, 253 (1974), with permission.]

4. Applications

A variety of reasons have been given for the numerous applications of thin layer techniques; however, there are two thin layer attributes in particular which have contributed to the widespread acceptance of these techniques. The first of these attributes, which has already been demonstrated in the theoretical section, is the relative simplicity of the descriptive equations. In addition, thin layer methods can provide exceptionally clean electrode surfaces. Since the working electrodes are exposed to a minimal amount of sample solution, the extent of contaminant adsorption on the electrodes is minimized.

In the following paragraphs, an attempt is made to present a representative sampling of the published applications. In addition to a very general discussion of each application, any unique characteristics making a thin layer cell particularly suited for a given experiment are given.

4.1. Measuring Rates of Associated Chemical Reactions

Several papers have been published^(19,24,49,50) describing the determination of rate constants for coupled chemical reactions by measuring steady-state current as a function of time.

4.1.1. Steady-State Current Decay—Twin Working Electrodes

Limiting steady-state currents (as obtained in the four electrode configuration) are directly related to the total concentration of electroactive species as indicated in Eq. (35). Thus for a chemical reaction involving either O or R , the rate constant can be evaluated by monitoring I_{ss}^{lim} . As discussed earlier, a limiting steady-state current is obtained when two facing working electrodes are held at potentials sufficiently cathodic and anodic to maintain zero concentrations of O and R at the respective electrodes (see part D of Figure 6). So for the reaction $O \xrightleftharpoons{ne} R \xrightarrow{k} P$, O and R can be considered to be cycling between the facing electrodes with R reacting occasionally to form electroinactive species P and thus being removed from the cycle (see Figure 22). The appropriate rate expression for this reaction scheme is

$$\frac{dc_P}{dt} = -\frac{dc_T}{dt} = kc_R \quad (36)$$

Using Eq. (35), the equal flux condition ($c_O D_O = c_R D_R$), and the preceding rate expression, the relation between the steady-state current and the chemical rate constant is found to be

$$\ln \left(\frac{I_{ss}^{lim}}{I_{ss,0}^{lim}} \right) = \frac{kt}{1 + (D_R/D_O)} \quad (37)$$

where $I_{ss,0}^{lim}$ is the limiting steady-state current initially.

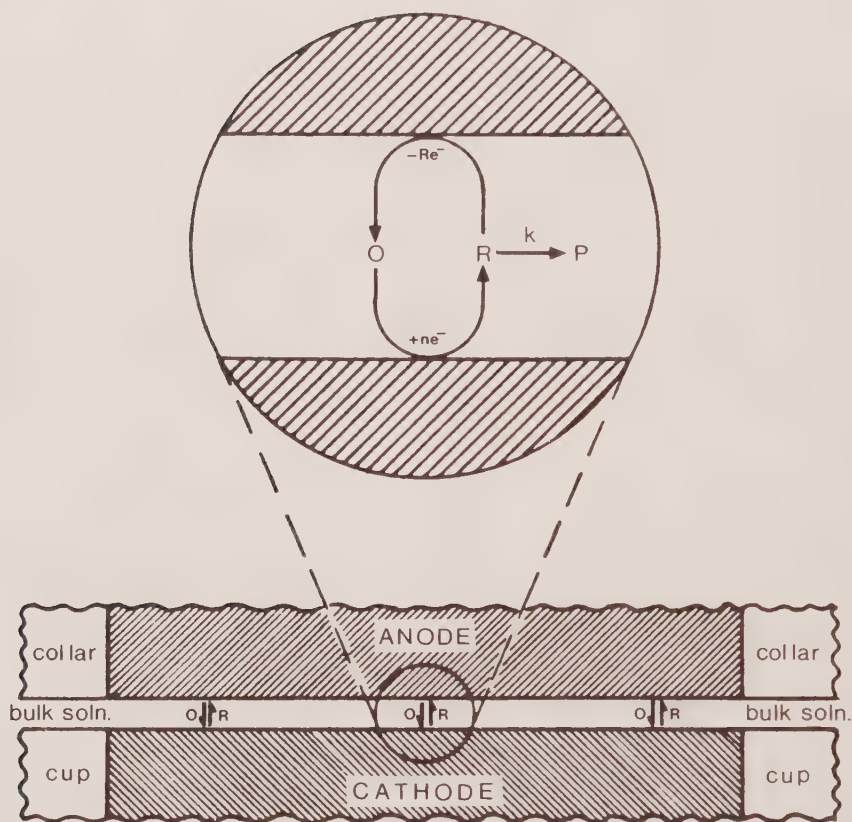
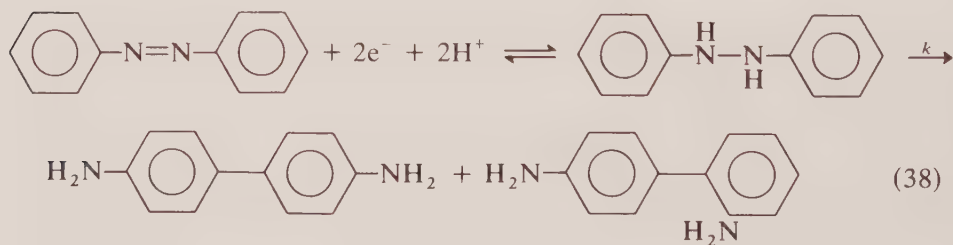


Figure 22. Schematic cross section of twin-electrode cell for steady-state current decay method.

An upper limit for the determination of k by this method is established by the requirement that the rate of mass transfer between the two working electrodes be much more rapid than the rate of the chemical reaction. On the other hand, the extent of edge effects into or out of the thin layer cavity sets the lower limit for k .

McDuffie *et al.*⁽²⁴⁾ used the steady-state current decay method to study the rate of the benzidine rearrangement under varying conditions of acidity. The reactions involved were



Their results, which are given in Figure 23, were in general agreement with those obtained by other electrochemical methods using identical solutions (i.e., 1 mM azobenzene, 0.25 *M* in ionic strength, and of sufficient acidity to maintain pseudo first-order conditions). The deviations from linearity at long times were accredited to edge effects.

4.1.2. Steady-State Current Decay—Catalytic Systems

A steady-state technique for determining the rate constant of a catalytic system such as



has been developed by Fleischman *et al.*⁽³²⁾ For a catalytic system in which the total amount of *X* plus *Y* remains constant, eventually the rate of production of *X* in solution must equal the rate of consumption of *X* at the electrode. Thus a steady-state current is obtained, the magnitude of which is related to *k*. This steady-state current results from an equilibration between a homogeneous and heterogeneous charge transfer process, not between two heterogeneous processes as discussed previously. Thus this experiment does not require a cell with two independently potentiostated working electrodes.

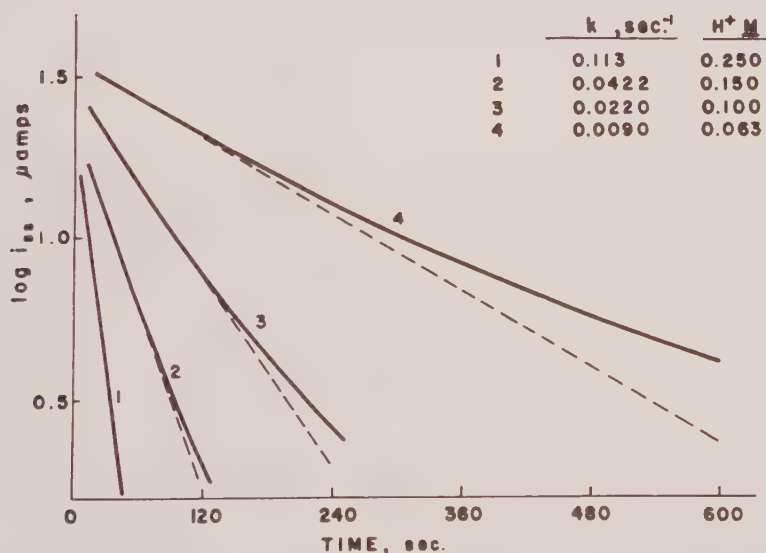


Figure 23. Steady-state current decay curves. — Experimental data; ---- limiting slopes. [Reprinted with permission from B. McDuffie, L. B. Anderson, and C. N. Reilley, *Anal. Chem.* **38**, 883 (1966). Copyright 1966, American Chemical Society.]

Equations for evaluating k from a plot of I_{ss} vs. ℓ are derived in Reference 32 and applied to the reactions of silver(II) in Reference 31.

4.1.3. Two-Step Methods

Non-steady-state methods which have been used to study EC reactions include two-step chronopotentiometry and coulometry experiments.^(15,51) In these methods a known amount of reactant is electrogenerated and allowed to react for a specified time. After that time, the amount of reactant remaining, which is measured electrochemically in a reverse step, is indicative of the rate of the chemical reaction. Since the species generated at the electrode cannot escape from the thin layer cavity, it is possible to extend this method to measure post-kinetic rate constants much smaller than those measurable with conventional semi-infinite electrochemical techniques. However, studying very rapid reactions ($t_{1/2} \leq 1$ sec) in thin layers is not particularly advantageous since diffusion effects must be considered.

4.1.4. Spectroelectrochemical Methods

Chemical kinetics have also been studied using spectroelectrochemical techniques.^(46,52) For example, one might generate a reactant electrochemically and then monitor the kinetics of the ensuing chemical reaction spectroscopically. If the kinetics of the chemical reaction are slow enough that the electrochemical generation of reactant can be considered instantaneous, then classical kinetic analysis can be applied to the absorbance vs. time results, rather than more complex transient electrochemical methods.

4.1.5. Cyclic Voltammetry

Laviron *et al.* have derived the descriptive equations for cyclic voltammograms obtained for reversible electrochemical reactions associated with a variety of irreversible chemical reactions. The cases considered include: EC mechanisms,⁽⁵³⁾ ECE mechanisms,⁽⁵⁴⁾ regeneration mechanisms,⁽⁵⁵⁾ and mechanisms in which a two-step electrochemical reaction is coupled to one or more chemical reactions.⁽⁵⁶⁾

4.2. Evaluating Diffusion Coefficients

Since the magnitude of a limiting steady-state current (in a four-electrode system) depends on the abilities of species O and R to diffuse back and forth between two parallel electrodes, this current contains information about the diffusion coefficients of O and R . To obtain absolute values for D_O and D_R requires a knowledge of ℓ and the O and R concentrations in the cell during the limiting steady-state current. The necessary concentrations are easily obtained spectrophotometrically or coulometrically.

When determining electrode concentrations coulometrically, one of the electrodes, say the cathode, is disconnected after a limiting steady state has been attained. If the current at the anode is then integrated, the total amount of R which was in the solution at steady state can be measured. An analogous experiment is then performed with the anode disconnected. Therefore, provided ℓ is known (e.g., from a coulometric calibration), D_O and D_R can be determined directly as shown in Eqs. (41 and 42).

$$D_O = - \frac{|I_{ss}^{lim}| \ell^2}{2Q_c} \quad (41)$$

$$D_R = \frac{|I_{ss}^{lim}| \ell^2}{2Q_a} \quad (42)$$

Here Q_c (a negative number) is the integrated current flowing at the cathode after disconnecting the anode. Since the exact magnitude of ℓ may be questionable and since D_O and D_R are extremely sensitive to the value of ℓ (second-order dependence), a more reliable number is the ratio of the two diffusion coefficients.

$$\frac{D_R}{D_O} = - \frac{Q_c}{Q_a} \quad (43)$$

This method has been demonstrated with Fe(II)–Fe(III) and quinone–hydroquinone systems by Anderson and Reilly.⁽¹⁸⁾ They point out that an advantage of this technique is that the steady-state current does not include a double layer charging component. Moreover, the steady-state concentration profiles presumed in the calculations are very stable toward disruption by convection due to the thinness of the layer.

4.3. Charge Transfer Rate Constant Determinations

As is evident in Eqs. (20–25, 33, and 34), sufficient information is available in both thin layer cyclic voltammograms⁽¹⁶⁾ and steady-state voltammograms^(8,18) to determine values for k° and α . Most of the few reported applications of thin layer techniques to this problem have been by Hubbard *et al.*^(57–59) They have used cyclic voltammograms to evaluate heterogeneous rate constants for a variety of platinum complexes.

4.4. Measuring Formal Potentials

Heineman *et al.*⁽⁶⁰⁾ described a simple spectroelectrochemical method for determining E° values which used less than a milliliter of solution. The method was applied to the redox enzyme, cytochrome *c*. Their technique is based on the fact that the concentrations of a redox couple, in equilibrium with a potentiostated electrode, are specified by the Nernst equation (see Eq. 1).

Since the system is at equilibrium, the electrode concentrations of O and R are equal to the bulk concentrations. Thus if the concentrations are measured spectrophotometrically at various applied potentials, $E^{\circ'}$ can be obtained from the intercept of a plot of $\ln(c_O/c_R)$ vs. E .

A critical point in this experiment was that the redox systems must have reached equilibrium before the concentrations were determined. When cytochrome c was the only electroactive species in solution, several hours were required to attain equilibrium due to the very slow rate of charge transfer between the enzyme and the electrode. The time required for system equilibration was reduced to five minutes or less by adding 2,6-dichlorophenolindophenol which functioned as an intermediate electron transfer agent between the electrode and the enzyme. Note that if conventional cells had been used, much longer electrolysis times would have been required to reach system equilibration.

4.5. *n*-Value and Concentration Determinations

Chronopotentiometry and potential step coulometry in thin layer cells have proven to be useful for determining either n -values or the concentrations of electroactive species in aqueous⁽³⁾ and nonaqueous solvents.⁽²⁷⁾ One of the advantages of these methods, as indicated in Eqs. (6–9), is that a knowledge of the diffusion coefficients is not required. A second advantage is that often Q and τ can be measured more precisely in thin layer cells than in conventional cells. This has been demonstrated by Christensen and Anson⁽³⁾ in a chronopotentiometric n -value determination for N,N -dimethyl- p -phenylenediamine. As shown in Figure 24, a sharper potential inflection occurs at the transition time in a thin layer cell than in a corresponding conventional cell. This has been attributed to the absence of a residual Faradaic current in the thin layer after the transition time and to the increased charge transfer reversibility resulting from smaller thin layer currents. Finally, these thin layer methods also have the advantage of virtually eliminating complicating secondary reactions between electroactive material diffusing into the electrode and products generated at the electrode.⁽³⁾ In studies of organic systems, this can be a welcome simplification.

Several other methods have been reported for measuring n -values or concentrations. Hubbard and Anson⁽⁶¹⁾ have determined n -values from cyclic voltammograms by measuring the areas under current peaks. (This area is directly related to charge provided the sweep rate is constant.) It has also been pointed out⁽¹⁷⁾ that for a charge transfer reversible system, since the peak current in a cyclic voltammogram has a second-order dependence on n (see Eq. 19), the current provides a very sensitive means of measuring n .

Very sensitive concentration determinations have been made using anodic stripping techniques in thin layers of solution.^(62–66) In this technique the metal ions of interest are deposited (by electrolysis) into a thin mercury film on the

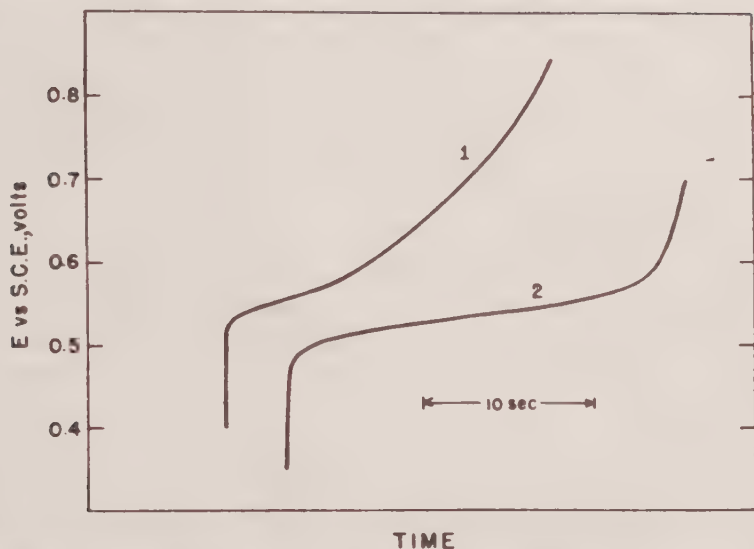


Figure 24. Chronopotentiograms for oxidation of *N,N*-dimethyl-*p*-phenylenediamine: (1) diffusion chronopotentiometry of $4.95 \times 10^{-3} F$ solution; current density, 0.6 ma. cm^{-2} ; (2) thin layer chronopotentiometry of $4.95 \times 10^{-3} F$ solution; current density 0.09 ma. cm^{-2} . Supporting electrolyte, 1 *F* H_2SO_4 . [Reprinted with permission from C. R. Christensen and F. C. Anson, *Anal. Chem.* **35**, 205 (1963). Copyright 1963, American Chemical Society.]

working electrode. The metals are quantified as they are stripped from the film using d.c. voltammetry,⁽⁶²⁾ second harmonic a.c. voltammetry,⁽⁶²⁾ or differential pulse voltammetry.^(63,64) Concentration determinations by stripping amalgam-forming metals from thin mercury films are more sensitive than when stripping from a mercury drop (since a more concentrated amalgam is formed) or from a glassy carbon working electrode.⁽⁶²⁾ Pb^{2+} detection limits reported for each of the stripping techniques are as follows: d.c. voltammetry—10 picograms,⁽⁶²⁾ second harmonic a.c. voltammetry—1 picogram,⁽⁶²⁾ differential pulse voltammetry—60 picograms (10 ng/ml for a 6 μl cell).⁽⁶⁴⁾

One of the principal advantages of the thin layer stripping technique is its ability to work with a small solution volume. In addition, since the entire volume of solution adjacent to the working electrode undergoes electrolysis, that small volume is used very efficiently. Perhaps the most important advantage over the conventional stripping technique is that all the metal ions can be deposited during electrolysis (assuming edge effects are negligible), thus eliminating errors due to variations in pre-electrolysis time, temperature, stirring rate, and potential. One disadvantage in using thin layer cells for concentration determinations is that the small volume of solution in the thin layer cavity must be determined accurately.

An inherent difficulty in using stripping voltammetry for multi-element analysis is the formation of intermetallic compounds when certain metals (e.g.,

Cu and Zn) are preconcentrated together on a working electrode. Using a thin layer cell with two independently potentiostated working electrodes, Heineman *et al.*^(64,65) have shown that by properly selecting the order and potential of electrolysis for each working electrode, interacting metals can be deposited on different electrodes, thus eliminating the interference.

4.6. Adsorption Studies

Adsorption processes which result in charge transfer (whether due to double layer restructuring or Faradaic processes) are usually detectable with electrochemical techniques. Described below are two techniques which have been used to study adsorption on platinum electrodes.

4.6.1. A Coulometric Method

Thin layer cells readily lend themselves to adsorption studies since the ratio of moles of electroactive species in the solution to that adsorbed on the electrode is minimal. As discussed below, the importance of this low ratio stems from the fact that adsorption is detected by measuring charge differences.

When an electroactive species adsorbs on the surface of the working electrode, the equation describing a subsequent coulometric experiment must be modified to account for deviations in the amount of reactant susceptible to electrolysis in the thin layer cavity.⁽¹⁰⁾ If the working electrodes are washed with an excess of the reactant solution before filling the cavity, and the adsorbed reactant remains electrochemically active, then for a cathodic process Eq. (44) applies.

$$-Q_c = nFVc_O^0 + nFA\Gamma_O + Q_b \quad (44)$$

If the reactant is not electroactive in the adsorbed form and the working electrodes are clean prior to filling the cavity (i.e., the electrodes are exposed to no excess of the reactant solution), then Q_c is given by

$$-Q_c = nFVc_O^0 - nFA\Gamma_O + Q_b \quad (45)$$

Several papers have been published concerning the adsorption of iodide and iodine on thin layer working electrodes.^(10,14,67) Using the techniques described in the preceding paragraphs, Hubbard *et al.*⁽¹⁰⁾ measured the number of moles of iodide or iodine on platinum electrodes in electroactive and nonelectroactive states.

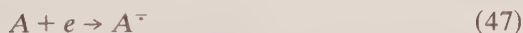
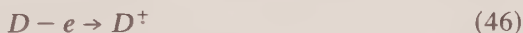
4.6.2. Cyclic Voltammetry and High Vacuum Techniques

The groups of Hubbard^(6,68) and Yeager⁽⁶⁹⁻⁷¹⁾ have used thin layer cells to obtain cyclic voltammograms for hydrogen adsorption on various crystal faces of platinum electrodes. In these experiments it is imperative that the

electrode surface be well characterized and relatively free of contaminants. Generally these experiments are done in high vacuum chambers to allow the use of techniques such as ion sputtering for electrode cleaning, LEED for determining electrode surface structure, and Auger spectroscopy for monitoring electrode surface composition. Thin layer cells are particularly appropriate for these experiments since with these cells only a minimal amount (typically 10^{-3} ml) of electrolyte need be introduced into the vacuum system. Moreover, since the electrode is exposed to only a small amount of solution, the likelihood of extensive surface contamination is small.

4.7. Investigation of Steady-State Electrogenerated Chemiluminescence

Using a thin layer cell with two independently potentiostated working electrodes, Bard *et al.*^(72,73) generated a steady-state chemiluminescence. The mechanism for this is as follows. As *A* and *D* diffuse to their respective electrodes, heterogeneous electron transfer occurs producing radical ions D^+ and A^- .



These radicals diffuse toward each other eventually meeting and reacting to give an excited species and one of the starting materials.



The excited species decays by emission of a photon, thereby regenerating the other starting material.



Any additional reactions which remove reactant from this cycle will limit the lifetime of the steady-state chemiluminescence.

As in steady-state voltammetry, concentration profiles are linear. However in the ECL cell, the zero concentration point for A^- and D^+ occurs somewhere in between the two working electrodes. The location of the zero concentration point (which is also where the chemiluminescence occurs) depends on the diffusion coefficients of A^- and D^+ and the concentrations of *A* and *D*. The working electrodes are usually potentiostated so that the concentrations of *A* and *D* are zero at the electrode where they are reacting.

There are several advantages in using the twin-electrode thin layer cells to electrogenerate chemiluminescence. One advantage is that a low d.c. voltage can be used to generate a steady-state chemiluminescence. In addition, since the system is at steady state there is no double layer charging (unlike the pulsed modes frequently used in conventional cells). Finally, since the two working electrodes are closely spaced, solution *iR* drops are minimized.

Unfortunately there are also a number of shortcomings with thin layer ECL cells. In fact, Bard concluded that thin layer cells were impractical sources of emission for an ECL device. (He preferred a flow cell.) One problem is that the emission leaving the thin layer cell is very weak. This is due in part to the fact that $A^{\cdot -}$ and $D^{\cdot +}$ must diffuse to the reaction zone, and in part to absorption by highly colored radical ions surrounding the reaction zone. A second problem which limits the lifetime of a thin layer ECL cell is that since there is so little solution in the thin layer cavity, it is extremely susceptible to impurities present initially or electrogenerated.

4.8. Underpotential Metal Deposition Studies

Schmidt and his group have published numerous papers on underpotential metal deposition.⁽⁷⁴⁻⁹⁰⁾ One particularly intriguing technique they have developed employs twin-electrode thin layer cells. In this cell configuration, there are two independently potentiostated electrodes on opposite sides of the thin layer cavity with auxiliary and reference electrodes located externally. (See Section 4.1.1.) One of the electrodes in the thin layer cavity (the generator electrode) is constructed from the metal (Me) which is to be deposited on the other electrode (the working electrode). The generator electrode acts as a reversible metal/metal ion (Me/Me^{z+}) electrode. Thus the metal ion concentration $[Me^{z+}]$ is related to the potential of the generator electrode as given by the Nernst equation. As the potential of the working electrode is varied (generally starting at a potential where essentially no Me has been deposited), the currents flowing through both the generator and working electrodes are recorded. The charge which flows through the generator electrode is that which is required to keep $[Me^{z+}]$ constant, and thus is directly related to Γ_{Me} , the surface concentration of Me at the working electrode. The charge which flows through the working electrode equals the charge due to the metal deposition process plus a double layer charging component due to the changing potential of the electrode. (The determination of the double layer charging component is discussed in the next paragraph.) The ratio of charge associated with the deposition process to the charge flowing through the generating electrode allows one to determine the electrosorption valency γ . (γ is the effective charge transferred through the external circuit per unit adsorption.)

The double layer charging component mentioned above can be determined to a first approximation by running a blank. The blank solution is easily obtained by potentiostating the generator electrode so that $[Me^{z+}] < 10^{-9} M$. Unfortunately the blank method is not completely correct, since during an actual deposition the potential of zero charge changes from that of the substrate metal to that of the deposited metal.

The applications presented here are certainly not all-inclusive; however, hopefully they do give the reader some indication of the wide spectrum of

problems that have been solved using thin layer techniques. Additional applications may be found in References 6–8.

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7

Tracer Methods in Electrochemical Studies

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Notation

A list of symbols used in this chapter with their definitions can be found on page 439.

1. Introduction

The advances in the studies on electrochemical systems made in the past 25 years are largely due to the development of new methods of investigation, including tracer methods. The first attempts to use tracer methods for metal/solution systems were made already at the beginning of this century by Paneth and Hevesy. However, tracer methods came to be widely used in electrochemical studies only rather recently when a large number of artificial isotopes became available. Essentially, the method consists in the following: trace amounts of an isotope of a particular element (tracer) in the same chemical form as the bulk of this element are introduced into the system, the behavior of the tracer being followed by means of radiometric and mass-spectrometric instruments. Assuming isotopic or radiation effects to be absent, the information on the behavior of the isotopic label is extended to that of the whole labeled substance. The method based on this principle is usually

called the tracer method. If radioactive isotopes are used, the method is known as the radioactive tracer technique or method.

The tracer method has a number of advantages: first, it allows the transfer of labeled substance from one phase to another or the increase of its concentration at the interface to be followed directly; second, it has a high sensitivity due to the fact that modern methods of radiometry and mass-spectrometry permit the detection of very small amounts of radioactive and stable isotopes ($\sim 10^{-10}$ g); third, the method shows a high specificity, which makes it possible to study the behavior of a labeled component in any system, however complex it may be. Moreover, the processing and interpretation of the experimental data obtained are relatively easy and it is possible to study electrochemical processes without their interruption.

In electrochemical studies isotopes have been most extensively used for investigation of the dissolution and deposition of metals, the evolution of hydrogen and oxygen, the adsorption of inorganic and organic substances, and the mechanism of electrocatalytic reactions.

The tracer method yields information on electrochemical systems which in principle cannot be obtained by any other methods. First, this applies to exchange processes between particles adsorbed on the electrode and the same particles in solution. These processes can be studied in detail by differential isotopic methods.[†] Second, this holds for determination of the anodic ionization currents of metals in the presence of much larger cathodic currents of ions discharged from the same metal, and vice versa.

In some cases the tracer method in combination with electric methods of measurement gives conclusive evidence on the mechanism of electrochemical processes. This has led to the solution of some fundamental problems of theoretical and applied electrochemistry.

A major contribution to the development of the tracer techniques in electrochemistry was made by the studies carried out in the laboratories of Professor K. Schwabe at Leipzig University, Academician A. N. Frumkin at the Institute of Electrochemistry of the Academy of Sciences of the U.S.S.R., Academician Ya. M. Kolotyrkin at the Karpov Institute of Physical Chemistry, Professor J. O'M. Bockris at the University of Pennsylvania, and Professor G. Horanyi at the Central Chemical Institute in Budapest.

The aim of this paper is to give the reader information on the possibilities of the tracer methods used in electrochemistry. For this reason, only those

[†] The differential isotopic methods consist essentially of consecutive adsorption of labeled and unlabeled adsorbate on the adsorbent surface, whereupon the kinetics of exchange of labeled adsorbate portions with the same, but unlabeled, adsorbate in solution are studied. Investigation of the dependence of the kinetics of this exchange on the sequence in which adsorbate portions are applied on the adsorbent surface makes it possible to decide whether the adsorption sites of the adsorbent surface are energetically uniform or nonuniform. The principles of differential isotopic methods are formulated by S. Z. Roginsky in his book *Adsorption and Catalysis on Inhomogeneous Surfaces*, Academy of Sciences of the U.S.S.R., Moscow (1948).

studies will be discussed which contributed in any way to the development of tracer techniques. The methods of investigation of the processes occurring in electrochemical systems under radiation (radiolysis, autoradiolysis) and of the behavior of the components of electrocatalytic systems present in radiochemical concentrations ($<10^{-6} M$), and the procedures for electrosynthesis of labeled compounds will not be considered here since these processes belong to a special branch of physical chemistry—namely, radiochemistry.

Naturally, the application of the tracer method in electrochemical systems is possible only if radioactive or stable labeled compounds with suitable characteristics are available. Particular attention should be given to the radiochemical and chemical purity of the isotopes used. Generally, experiments with the use of radioactive isotopes require specially equipped rooms.

2. Methods Used for Investigation of Adsorption Processes

The adsorption of ions and molecules on electrodes affects significantly the kinetics of electrochemical reactions. Generally, one of the stages of electrochemical transformation of a substance is the adsorption of reactant or intermediate products on the electrode. The understanding of the mechanism of these transformations requires information on the electric double layer structure, which gives insight into the origin of a potential difference at the interface. Therefore the investigation of adsorption and of the electric double layer composition and structure is one of the main tasks of electrochemistry.

The modern radioactive tracer methods used in such investigations can be divided into three groups. The first group includes methods based on the determination of the change of the labeled adsorbate concentration in solution; the second involves methods based on the determination of the radioactivity of the substance adsorbed on the electrode after removal of the electrode from solution; and the third group includes methods based on the determination of the radioactivity of the substance adsorbed on the electrode immersed in solution.

2.1. Determination of the Change of the Adsorbate Concentration in Solution (the "Solution" Method)

When a substance undergoes adsorption on the electrode its concentration in solution changes. If the adsorbate is labeled with a radioactive tracer, in order to find the extent of adsorption on the electrode it is necessary first to determine the radioactivity of some small solution volume I^0 (pulse/min), then to immerse the electrode into the solution, to keep it there under given conditions, and to determine again the radioactivity of the same solution volume I_1 (pulse/min).

If we know the total solution volume $V(\text{ml})$ from which adsorption occurred, the adsorbate concentration $C(\text{g.-mol/ml})$ determined independently and the true surface of the electrode $S(\text{cm}^2)$, we can calculate the extent of adsorption by means of the formula

$$\Gamma = \frac{I_0 - I_1}{I_0} \cdot \frac{C \cdot V}{S} (\text{mol/cm}^2) \quad (1)$$

The error in the determination of the quantity Γ depends on the relative change of the adsorbate concentration in solution $(I_0 - I_1/I_0)$ and on the accuracy of the radioactivity measurements (of the quantities I_0 and I_1). (The quantity I_0 should be much larger than the natural counter background.) The error in the determination of Γ is usually 10–15%. Thus, e.g., if the relative change of the adsorbate concentration is 20% and I_0 and I_1 have been determined with an accuracy of $\pm 2\%$, the error in the determination of Γ is $\geq 15\%$. In each particular case the error can be estimated by means of the formula generally used for determination of the accuracy of tracer measurements.

The minimum change of adsorbate concentration (%) which can be recorded with sufficient accuracy by radioactivity measurements is the sensitivity of this method and is equal to $\sim 10\%$ (rarely 5%) of the value of I_0 . At $I_0 - I_1/I_0 = 0.1$ (or 10%), we obtain for the sensitivity of the method the quantity $0.1 \cdot C \cdot V/S$, from which it follows that it is possible to enhance the sensitivity by decreasing the ratios V/S , on one hand, and by increasing the accuracy of the measurement of the quantities I_0 and I_1 , on the other hand. Under favorable conditions, by means of the "solution" method it is possible to measure reliably the extent of adsorption corresponding to 10^{-10} – 10^{-11} mol/cm² true surface.

In the simplest version the adsorption determination by the "solution" method amounts to measuring the radioactivity of solution samples. However, this involves a change in the adsorbate volume, which leads to violation of the constancy of the experimental conditions and limits the number of individual radioactivity measurements. At present two versions of the "solution" method are used which allow determination of the radioactivity of the solution without changing its volume. In the first version, part of the solution is introduced into a special measuring cell connected with the main cell in which adsorption occurs. After the radioactivity measurement, the solution returns to the main cell. The solution can be brought into the measuring cell at regular intervals (Figure 1), or can be circulated by means of a centrifugal pump between the main and the measuring cells (Figure 2). In the second version, the wall or the bottom of the main cell is made from thin glass or thin (10^{-4} m) inert polymeric material. A radioactivity counter is placed in the immediate vicinity of the cell wall or bottom from the outside (Figure 3).

A device of original design was proposed for measuring the adsorption of iodine ions on iron by the "solution" method (Figure 4).⁽¹⁾ In this device

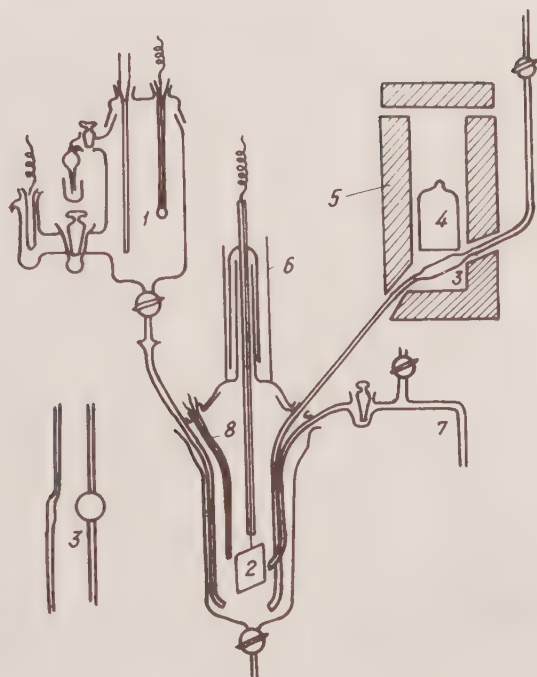


Figure 1. Adsorption measurement by the "solution" method: (1) cell for preparation of solution, (2) metal specimen (working electrode), (3) cell for radioactivity measurement, (4) radiation counter, (5) lead shield, (6) hydraulic gate, (7) gate for potential measurement, (8) auxiliary electrode.⁽¹¹⁾

the electrode was iron electrolytically deposited on platinum sputtered on the inside surface of a cylindrical glass tube. The ratio between the solution volume and the adsorbent surface was advantageous, which made it possible to measure the adsorption of iodine ions with a small true surface of the electrode from 10^{-3} M NaI solution.

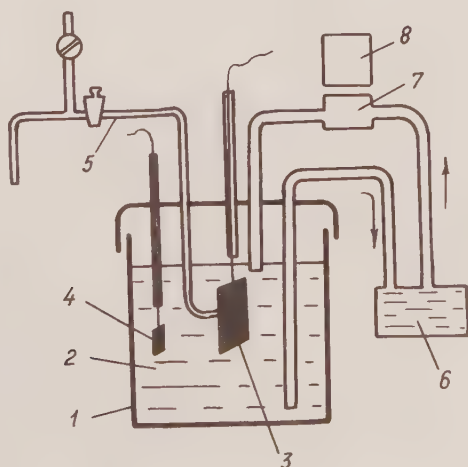


Figure 2. Adsorption measurement by the "solution" method with solution circulation: (1) cell body, (2) adsorbate solution, (3) working electrode, (4) auxiliary electrode, (5) bridge for potential measurement, (6) pump, (7) cell for measuring the solution radioactivity, (8) radiation counter.

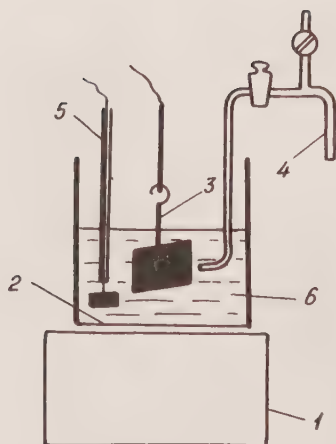


Figure 3. Adsorption measurement by the "solution" method: (1) radiation counter, (2) membrane, (3) working electrode, (4) bridge for potential measurement, (5) auxiliary electrode, (6) adsorbate solution.

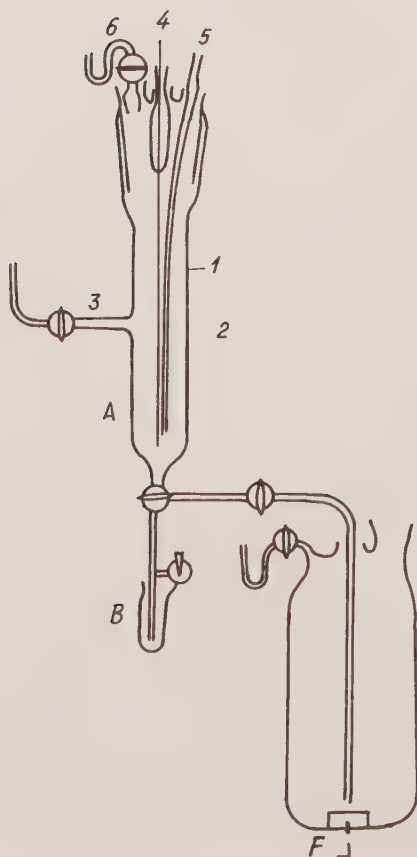


Figure 4. Adsorption measurement by the "solution" method: (A) adsorption vessel with a cylindrical iron electrode, (1) electrode, (2) electric contact, (3) capillary for potential measurement, (4) auxiliary electrode, (5) connection to helium or vacuum system, (6) gas outlet, (B) vessel for measuring the solution radioactivity, (F) magnetic stirrer.⁽¹⁾

The design of the cells used for the radioactivity measurements of the solution is defined mainly by the kind of radiation emitted by the isotopic label and should ensure the maximum sensitivity of the counter to radiation. If hard β - and γ -radiators are used, it is possible to employ only the first version of the "solution" method (see Figures 1, 2). With soft β -radiators the second version is more suitable (see Figure 3). If radiation analyzers are used, it is possible to study simultaneously the adsorption of several radioactive substances. To avoid errors due to adsorption on the cell walls it is necessary to know the adsorption properties of the cell material.

The "solution" method of adsorption measurements makes it possible to determine the extent and kinetics of adsorption (desorption) and exchange as a function of temperature, electrode potential, adsorbate concentration, solution composition, and adsorbent preparation. With effective stirring of the solution, the first version of the method, with solution circulation, and the second version can be used for investigation of fairly fast desorption and adsorption processes. Both versions can be made automatic.

When desorption and adsorption processes are studied, the adsorbate solution is renewed and the transition of the adsorbed substance from the electrode into solution is recorded from the increase in the radioactivity of the latter. The accuracy of these measurements is much higher than that obtained when investigating the adsorption of labeled adsorbate since measurements are performed in the presence of a small radioactive background.

The limitations of the "solution" method are low sensitivity and poor accuracy. It is possible to use this method only when the adsorption capacity of the adsorbent ($\Gamma \cdot S$) is no less than 10% of the total adsorbate content in solution. For this reason, most of the studies by this method were carried out on electrodes with a highly-developed surface at adsorbate concentrations no higher than 10^{-2} M. At adsorbate concentrations of 10^{-5} – 10^{-4} M the method can be used for investigation of adsorption on smooth metals when the extent of adsorption per 1 cm^2 true surface is $\sim 10^{-9} \text{ mol/cm}^2$.

It should be noted that in the adsorption measurements by the "solution" method, the adsorbate concentration in solution does not remain constant due to various factors. When the dependence of the extent of adsorption on the electrode potential is studied by the "solution" method, the measured dependence will be close to that sought only if the extent of adsorption depends slightly on potential. Otherwise the difference between the dependences measured and sought becomes appreciable since at different potentials adsorption occurs from solutions of different concentration.

If it is necessary that the initial and final adsorbate concentrations should be equal, the solution should be renewed and the change in the concentration of each new portion be taken into account. However, this complicates measurements and reduces the accuracy of the determination of the extent of adsorption. The low accuracy of the "solution" method is due to the fact that it

involves the recording of small radioactivity changes in the presence of a large radioactive background.

In the case of electrodes with a highly-developed surface, the "solution" method was used for investigation of ion adsorption on iron,⁽²⁾ chromium,⁽³⁾ platinized carbon,⁽⁴⁾ platinized platinum,⁽⁵⁾ sponge lead,⁽⁶⁾ and nickel powder.⁽⁷⁾ The "solution" method has yielded the best results for the adsorption of iodine ions on smooth silver from diluted solutions.⁽⁸⁾

The "solution" method has been described earlier in References (9)–(12). Due to the limitations outlined above, it has not come into wide use.

2.2. Determination of the Radioactivity of the Specimen after Its Removal from Solution (the "Electrode" Method)

The method of adsorption determination from the radioactivity of the electrode removed from solution consists of the following operations. The electrode is placed into the labeled adsorbate solution and kept under given conditions; then the process is interrupted, the electrode is removed from solution, and its radioactivity is measured. The absolute value of the extent of adsorption is determined by comparing the radioactivity of the specimen with a radioactive standard. The extent of adsorption is calculated by means of the formula

$$\Gamma = \left[\frac{(I_1 + I_2) - I_s}{2 - 0.01 K} \right] \cdot \frac{c}{I_{sp} \cdot S} \text{ (g.-mol/cm}^2\text{)} \quad (2)$$

where Γ is the extent of adsorption, C is the adsorbate concentration (mol/mL), S is the true electrode surface (cm^2), I_{sp} is the specific radioactivity of the solution (expressed in pulse/min mL), I_1 and I_2 are the measured radioactivities of the two sides of the electrode (pulse/min), K is the radiation absorption coefficient in the specimen (%), and I_s is the radioactivity of the solution layer wetting the electrode (pulse/min).⁽⁹⁾

The absorption coefficient K is found experimentally. For this purpose a drop of labeled solution is deposited on one of the sides of the electrode and dried. Then its radioactivity is measured (I_1^*) as well as the radioactivity of the opposite side of the electrode (I_2^*). From the obtained radioactivity values, K is calculated from $K = I_1^* - I_2^*/I_1^* \times 100\%$. The coefficient K depends on the electrode material density (g/cm^2), and the kind and energy of radiation. To correct for absorption the quantities $(2 - 0.01 K)$ or $(1 + K_1)$ (where K_1 is the radiation transmission coefficient equal to I_2^*/I_1^*) can be used. If the electrode practically completely absorbs the radiation, the sum of the radioactivities of the two sides of the electrode is used in the calculation.

I_{sp} is determined by measuring the radioactivity of a portion of adsorbate solution under the same geometric conditions as in measuring the radioactivity of the electrode covered by adsorbed substance. For this purpose a solution

drop is deposited on the electrode and weighed in a closed vessel, whereupon its radioactivity is measured. From the weight of the drop and its radioactivity, the radioactivity of 1 mL of solution (I_{sp}) is calculated. In determinations of the radioactivity of an undried drop, systematic errors may arise, associated with the nonuniform distribution of the drop over the electrode surface, on one hand, and with the absorption of part of the radioactive radiation in the solution layer, on the other hand. In determining the radioactivity of a dried drop, errors may arise due to nonuniform distribution of the dry deposit over the electrode surface, which leads to partial weakening of radiation, and due to decrease of radioactivity caused by formation, upon drying, of aerosols and volatile compounds containing labeled adsorbate. The errors in the radioactivity determination of a dried drop can be allowed for but this requires additional measurements.⁽¹³⁾ To eliminate these errors it is necessary, after weighing the drop, to convert adsorbate into an insoluble compound (if possible) and, when drying the drop, to add to the solution a small amount of insulin,⁽¹⁴⁾ or to apply some other methods to achieve a more uniform distribution of the deposit.

After removal from solution, the metal electrode contains adsorbate in adsorbed state and in the wetting solution layer (I_s). If their amounts differ little, it is possible to measure the radioactivity of the electrode after drying the solution[†]) present on the electrode and then introduce a correction for I_s on the basis of the weight of the solution wetting the electrode and its specific radioactivity, as was suggested in Reference 9. If $(I_1 + I_2) \gg (I_s)$, then it is not so important to introduce the correction. If, however, the amount of adsorbate in the wetting layer is greater than that of adsorbed substance, the determination of the extent of adsorption is not accurate. In such a case it is necessary to remove the wetting solution layer with the use of filter paper or by washing the electrode in liquids. As a rule, this procedure is used for electrodes from smooth metals. It is possible that, during washing of the electrode, part of the adsorbed substance may be removed from it, which must be allowed for in calculating the extent of adsorption. When metals with a highly developed surface are used, such as platinized platinum, the extent of adsorption can be determined accurately enough without washing the electrode even at adsorbate concentrations of $10^{-2} M$.

The sensitivity of the method is defined by the minimum number of pulses recorded with a given accuracy and by the specific radioactivity of the solution (pulse/min mol). The sensitivity is higher, the greater the specific radioactivity of solution.

The accuracy of the method is defined by the error in the measurement of the quantities I_1 , I_2 , and I_{sp} , being usually $\pm 10\%$. Relative measurements can be performed with a much better accuracy (1–2%).

[†] During drying of the electrode, the radioactivity should not decrease through evaporation of volatile compounds or aerosol formation.

The advantages of the "electrode" method of measuring adsorption are the simplicity of measurements, high sensitivity, and the possibility of using isotopes emitting any kind of radiation.

The method has also a number of significant drawbacks. The adsorption measurements require interruption of the adsorption process. When the electrode is taken out from solution into the air and the solution is washed off, the measurements become indeterminate with respect to the electrode potential and adsorbate concentration since it is possible that not only the wetting solution layer but also part of the adsorbed substance may be removed. The method is time-consuming due to the necessity of special preparation of the electrode before each measurement.

In view of the disadvantages mentioned, the method yields the most reliable results in studies of strong chemisorption on metals at the potential acquired by the electrode in air. In some cases, by using a redox system which imposes its potential on the electrode, it is possible to obtain reliable adsorption data at other potentials.^(15,16)

The method as described allows one to measure the extent and to study the kinetics of strong adsorption as a function of various factors, and also to follow the exchange between an adsorbed substance and the same substance in solution.

In spite of its limitations, the "electrode" method was formerly widely used for investigation of ion adsorption on metals with a highly developed surface, in particular, on platinum, rhodium,^(12,15-24) and palladium,^(25,26) for investigation of the adsorption of organic substances on iron, nickel, copper, and other metals,⁽²⁷⁻³⁰⁾ and for adsorption studies on semiconductors.⁽³¹⁻³³⁾

The "electrode" method was used also for detection of the penetration of adsorbed ions into the metal bulk⁽³⁴⁻³⁶⁾ and in the recording of radiation by the autoradiographic method⁽³⁷⁾ in studies on the distribution of adsorbate over metal surface.^(36,38)

The method in question was used also for investigation of the adsorption on platinum of tritium-labeled water in the system Pt-1 N H₂SO₄. In that case the electrode was subsequently washed in acetone.⁽³⁹⁾ It was found, however, that the method could not be used for that purpose⁽⁴⁰⁾ since, on one hand, it does not allow for control of the completeness of removal of tritiated water present in the solution layer wetting the electrode and, on the other hand, the amount of adsorbed water is affected by acetone adsorption on platinum during washing.

At present, in many cases the "electrode" method has given way to more refined methods (which will be described in the next section), an exception being the studies on the adsorption processes of ions and organic substances in the range of high anodic potentials, where the "electrode" method has proved to be especially successful.

The application of the "electrode" method led to a number of important scientific results. Thus by this method strong adsorption of HSO₄⁻, Cl⁻, Br⁻,

and I^- ions on smooth platinum at potentials of about 2.0 V was proved.⁽⁴¹⁻⁴⁵⁾ The use of a rotating disc electrode in the measurements in the range of high anodic potentials allowed elimination of diffusion difficulties, as well as the difficulties associated with vigorous gas evolution. The method was used to measure the adsorption of organic compounds on platinum at potentials in the range of 1.5–3.5 V.⁽⁴⁶⁻⁴⁸⁾ The technique of the measurements was further developed in References (49) and (50), where, due to a special design of cooled electrodes (Figure 5), the adsorption of sulfuric, phosphoric, and acetic acid anions could be measured up to a potential of 4.0 V. The main limitation of these measurements is that it is impossible to determine the total extent of adsorption as it is necessary to wash the electrode.

It should be borne in mind that due to the different bond strengths of adsorbed particles at different potentials, the extent of adsorption measured after washing the electrode depends not only on the initial extent of adsorption, but also on the washing time, as can be seen from the data in Figure 6.⁽⁵⁰⁾ This can account for the differences in the data on the adsorption of substances in the range of high anodic potentials obtained by electrochemical and radio-active tracer methods (Figure 7).⁽⁴⁸⁾

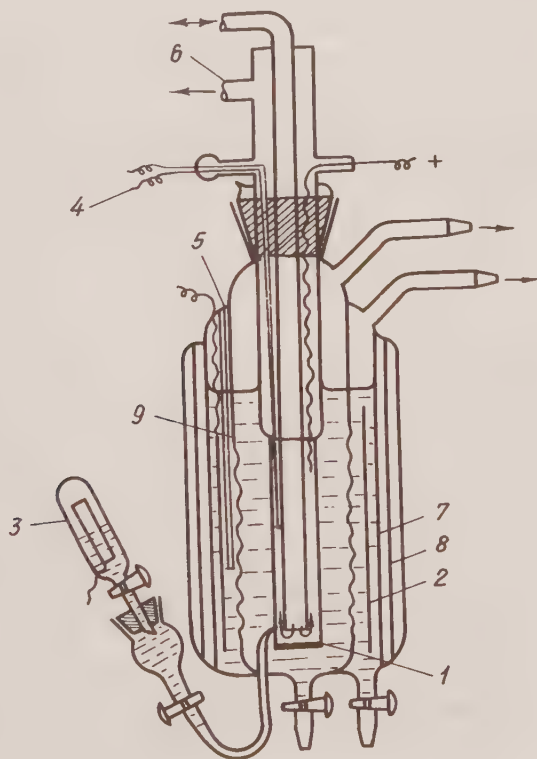


Figure 5. Electrolyzer with cooled Pt anode: (1) complete Pt anode, (2) Pt cathode, (3) reference electrode, (4) thermocouple for determination of anode temperature, (5) thermocouple for determination of cathode temperature, (6) supply of refrigerant to anode, (7) electrolyzer jacket, (8) vacuum jacket, (9) porous glass diaphragm.⁽⁴⁹⁾

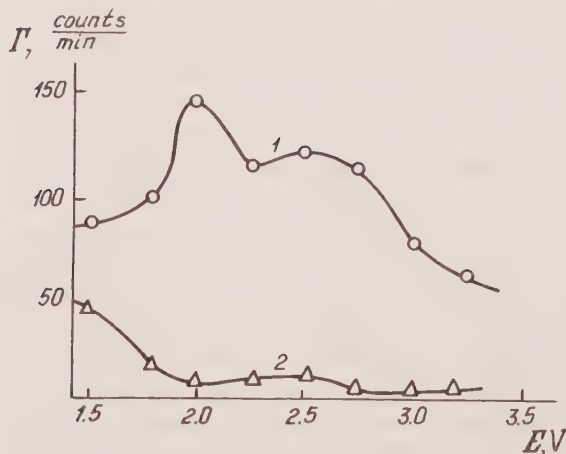


Figure 6. Dependence of the extent of adsorption of acetate ions on the platinum electrode potential measured (1) after 15-minute washing of electrode in supporting electrolyte solution and (2) after 5-minute polarization of electrode in unlabeled adsorbate solution.⁽⁵⁰⁾

For the present, the "electrode" method is the only radioactive tracer method used for the investigation on smooth metals of the adsorption processes occurring at high current densities and involving a considerable heating of electrolyte and vigorous gas evolution.

A new version of the "electrode" method—the "tape" method—was proposed by Green, Swinkels, and Bockris.⁽⁵¹⁾ In their opinion this method is free of the drawbacks of the versions described earlier. In particular, it allows the measurement of the extent of adsorption as a function of potential without interrupting the process and removing the electrode from the solution into

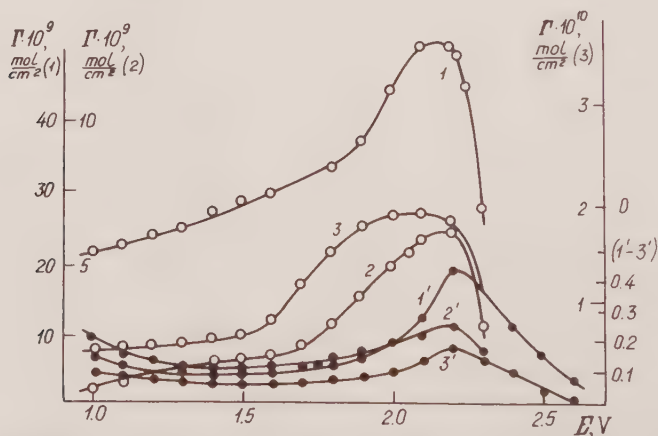


Figure 7. Dependence of adsorption Γ (Curves 1-3) (data of radioactive tracer measurements) and coverage θ (Curves 1'-3') (data of electrochemical measurement) on potential: (1), (1') benzene, 8.9×10^{-2} mole/L; (2), (2') naphthalene, 2×10^{-4} mole/L; (3), (3') benzene, 10^{-2} mole/L.⁽⁴⁸⁾

air. Briefly, this method consists of the following. A closed metal tape acting as an electrode rotates by means of rollers and on leaving the solution, by means of a special device, is freed of the solution layer wetting it. The radiation counter is located under the tape outside the solution. The complete set-up is placed in a chamber under an inert gas atmosphere. The thickness of the liquid layer and hence the amount of radioactive substance in it is calculated from the change in the capacity of a capacitor between whose plates the tape is passed.

This version of the method has a number of significant drawbacks. It is applicable only to isotopes with α and soft β radiations and cannot be used for determination of volatile adsorbate adsorption. Important errors may arise in the measurements associated with the inaccuracy of the correction for the wetting solution layer and with the inaccuracy of the control of the electrode potential (after the tape leaves the solution its potential cannot be controlled).

The "tape" method was used for investigation of the adsorption of organic substances on copper, nickel, iron, lead, and platinum.^(52,53) However, the error associated with the correction for the wetting solution layer proved to be too large and therefore the reliability of the results obtained by the "tape" method is questionable. For this reason the "tape" method is practically not used at present.

2.3. Determination of the Radioactivity of the Adsorbate on the Electrode Immersed in Solution

The adsorption of labeled substance leads to increase of the radioactive surface layer. The methods based on the utilization of this effect can be divided into three sub-groups: the "foil" method, the "thin layer" method, and the "electrode lowering" method.

2.3.1. The "Foil" Method

The principle of this method was proposed by Frederick Joliot⁽⁵⁴⁾ and involves the following. A thin metal foil forms part of the cell in which labeled solution is contained. Upon contact with solution its inner side adsorbs labeled substance. The radiation counter is located directly at its outer side. By this method Joliot and, later, other authors studied the electrodeposition of radioelements. Annianson⁽¹³⁾ suggested that the method could be used for investigation of the adsorption from solutions with adsorbate concentration up to 10^{-3} M. Weissmantel seems to have been the first to carry out such measurements. Instead of metal foil in his experiments he used a thin layer of platinum sputtered on mica under vacuum, which served as the bottom of a cell made from Plexiglas. In one of the versions of the method the adsorption was measured directly after sputtering the metal on mica under vacuum, which made it possible to start adsorption measurements on the metal free of adsorbed

oxygen. In these studies the radiation intensity was automatically recorded and radiation analyzers were used for simultaneous measurement of two substances containing different labels. Serious drawbacks of these studies were insufficient experimental purity (organic glue was used, etc.) and the absence of control of the metal potential.

An improved version of the method under consideration allowing adsorption to be measured at a controlled potential was proposed by Blomgren and Bockris.⁽⁵⁵⁾ In their experiments a thin gold foil (~ 1 micron) was used as metal specimen. It was attached to a metal grid forming part of a flowing-gas counter mounted over the solution surface in such a manner that the solution surface and the foil remained parallel when the counter was moved in the vertical direction. As the counter approached the solution its radioactivity was measured as a function of the distance. When metal comes into contact with solution, the radioactivity being measured increases sharply due to the adsorption on metal. The radioactivity value of the adsorbed substance is the difference in the radioactivity values measured after and before the contact of the electrode with solution. This device is illustrated schematically in Figure 8. The above version of the "foil" method was used for investigation of the adsorption of thiourea,⁽⁵⁵⁻⁵⁷⁾ naphthalene, benzene, and phenanthrene^(58,59) on gold, and ethylene,^(60,61) benzene,⁽⁶²⁾ phenol,⁽⁶³⁾ butane,^(64,65) and methanol⁽⁶⁶⁾ on platinized gold.

One more version of the "foil" method was developed recently by Horanyi.^(67,68) The schematic of the cell is shown in Figure 9. In his experiments, metal (gold) was sputtered on a polymer film stretched over a special glass head. This allows an easy replacement of the electrodes, which is not possible in the Blomgren-Bockris version. Using this version of the method, Horanyi and collaborators carried out a series of studies on the adsorption of inorganic⁽⁶⁸⁻⁷¹⁾ and organic substances.⁽⁷²⁾ In their experiments they used a scintillation counter. A device of similar design was used by Polish authors⁽⁷³⁾ for investigation of methanol adsorption. Apparently they achieved a higher sensitivity of radioactivity measurements than other investigators owing to

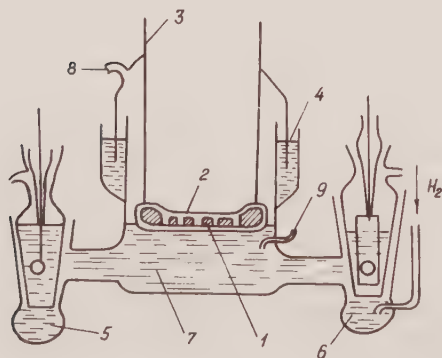


Figure 8. Cell for adsorption measurement by the "foil" method: (1) working electrode, (2) counter window, (3) counter wall, (4) hydraulic gate, (5) auxiliary electrode, (6) reference electrode, (7) adsorbate solution, (8) gas inlet, (9) introduction of solution sample.⁽⁵⁷⁾

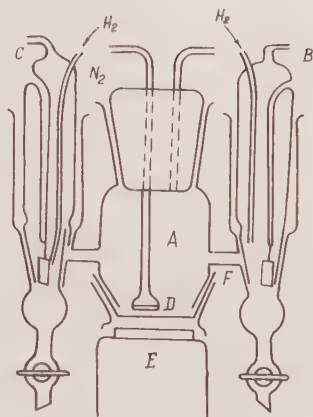


Figure 9. Cell for adsorption measurement by the "foil" method: (A) working volume of the cell, (B) reference electrode, (C) auxiliary electrode, (D) working electrodes, (E) radiation counter, (F) electric contact from the working electrode.⁽⁶⁷⁾

application of liquid-cooled scintillators. This technique makes it necessary to conduct experiments in the dark, which complicates them.

The electrodes used in the subgroup of the methods under discussion must satisfy a number of requirements: first, they must be strong enough since they serve as the cell bottom; second, they must be thin enough in order that α and β particles pass through them without significant absorption. Therefore, in each particular case, depending on the kind of radiation emitted by the isotopic label, the adsorbate concentration, and other factors, it is necessary to choose some optimum version which ensures the greatest sensitivity and accuracy of measurements.

The theoretical principles of the methods of the subgroup considered are presented in References 57, 67, and 68.

In the general case, the radioactivity measured by the counter (I_u) is the sum of two quantities: the radioactivity of adsorbed substance (I_a) and the radioactivity of adsorbate in solution (I_p):

$$I_u = I_a + I_p \quad (3)$$

It is assumed that the adsorbate concentration in solution before and after adsorption remains unchanged (practically constant). In the case of ion adsorption, the diffuse part of the adsorption layer is usually neglected since the correction for it is small as a rule. In any case it can always be estimated using, for instance, the "mixed electrolyte" method.⁽⁷³⁻⁷⁶⁾

The radiation intensity of adsorbed substance is expressed as

$$I_a = \lambda \Gamma \quad (4)$$

and the radiation intensity of solution as

$$I_p = \lambda \bar{c} \int_0^\infty e^{-\mu x} dx = \lambda \frac{\bar{c}}{\mu} \quad (5)$$

whence it follows that

$$I_u = \lambda \left(\frac{\bar{c}}{\mu} + \Gamma \right) \quad (6)$$

where $\lambda = AI_0\beta$, A is the geometrical surface of the electrode, I_0 is the specific radioactivity of labeled adsorbate expressed in Curie/mole, $\bar{c}$ is the adsorbate concentration expressed in mole/mg, β is the counting efficiency, μ is the mass absorption coefficient in cm^2/mg , and x (mg/cm^2) is equivalent to the distance from the electrode. β includes the geometrical efficiency, the absorption of radiation by the electrode, and the counter efficiency. For convenience, the mass absorption coefficient (μ), which is independent of the nature and density of the medium, is expressed in cm^2/mg .

When the roughness (γ) is other than unity, the expression for I_u is of the form:

$$I_u = \lambda \left(\frac{\bar{c}}{\mu} + \gamma\Gamma \right) \quad (7)$$

Using this expression, the potentialities of the method can be assessed. The systematic error is defined mainly by the relation between $\bar{c}/\mu$ and $\gamma\Gamma$. Evidently, increase of γ and μ and decrease of $\bar{c}$ will favor the decrease of the error. It should be borne in mind that with increase of γ , usually associated with increase of the adsorbent thickness, the counting efficiency decreases.

To determine I_a it is necessary to find I_p , which can be done by several methods. The simplest and most reliable method is as follows: a portion of solution is prepared in which the label concentration is the same as in the solutions being investigated, and the concentration of the stable preparation is much higher (~ 10 times). In this case the measured radioactivity practically coincides with I_p since, due to its small contribution, the radioactive preparation is scarcely adsorbed on the electrode.⁽¹³⁾ When measurements are performed on metals sputtered on mica (or polymer film), the radioactivity value of the solution can be measured also in the following way: with its smooth side, mica is turned toward the solution and with the sputtered metal layer, toward the counter. Then the cell is filled with the solution. Ignoring the adsorption on mica, we can assume the adsorption being measured to correspond to the solution radioactivity in the adsorption experiment.^(18,20)

In the Blomgren-Bockris version⁽⁵⁵⁾ I_p is determined by extrapolation to zero distance of the dependence of the radioactivity value being measured on the distance between electrode and solution. However, this method is less accurate than the one described above since extrapolation to zero distance is performed with a low accuracy.

In another procedure, from independent measurements the conditions are found under which the adsorption is close to zero and the radioactivity is measured under these conditions, then $I_u = I_p$ ⁽⁶⁸⁾ I_p can be found also by

measuring, under the same conditions as in the main experiment, the radioactivity of the solution containing the substance labeled with the same isotope as the substance being investigated, but which is not adsorbed on the electrode. The specific radioactivity (Curie/mole) of this other substance should coincide with that of the solution being investigated. Thus, in studying the adsorption of organic substances labeled with the isotope ^{14}C , $\text{Na}_2^{14}\text{CO}_3$ was used as a standard.⁽⁵⁵⁾

Usually for calculation of the absolute values of the extent of adsorption, I_a is compared with the radioactivity of the standard, which is measured under the same conditions. The solution itself can serve as a standard if its specific radioactivity is known. This procedure was proposed for calculation of the extent of adsorption by Wroblowa and Green.⁽⁵⁷⁾ Let us express I_p and I_a as

$$I_p = 3.7 \times 10^{10} \alpha c S K \int_0^\infty \exp(\mu x) dx \quad (8)$$

$$I_a = 3.7 \times 10^{10} \Gamma_M \alpha \theta S K \gamma \quad (9)$$

where α is the specific radioactivity of the solution (Curie/mole), c is the concentration (mole), S is the electrode area (cm^2), μ is the radiation absorption coefficient (cm^{-1}), x is the distance from the electrode into the solution bulk (cm), K is the counting efficiency coefficient, Γ_M is the adsorbed amount corresponding to a monolayer (mole/cm^2), θ is the coverage, and γ is the roughness equal to the ratio of true to visible surface. It follows from the expression for I_a and I_p that

$$I_a = I_p \Gamma_M \theta \gamma \mu c^{-1} \quad (10)$$

If we know γ , Γ_M at $\theta = 1$ and μ , it is possible to calculate I_a corresponding to a monolayer coverage. Hence it is easy to find θ for any I_a .

It should be borne in mind that the determination of Γ_M and γ always involves some assumptions and this fact should be taken into consideration in calculating Γ . For instance, in determining Γ_M it should be agreed which quantity is to be taken for an adsorbed substance monolayer: the maximum amount of substance adsorbed under experimental conditions or the amount of adsorbed particles numerically equal to the number of adsorbent surface atoms. In determining γ it should be agreed what is to be taken for true surface. Thus, in calculating γ by the BET method from krypton adsorption, the adsorbent surface participating in krypton adsorption is taken to be true surface.

The main advantage of the methods described is the possibility to take measurements without interrupting the process, which allows, in particular, automation of the recording of the radiation intensity. Another advantage is that it is possible to begin recording with very small time intervals after contact is established between solution and metal. However, in such cases the error may be large, especially when using dilute solutions, as the result of the

concentration decrease at the initial moment in the solution layer immediately adjacent to the electrode.

The "foil" method can be used for investigation of the kinetics of adsorption, desorption, and exchange of adsorbed substance with the same substance in solution. With the use of this method it is possible to measure the dependences of the extent of adsorption on the electrode potential, adsorbate concentration, and temperature.

The application of this subgroup of methods is limited primarily by the necessity to use isotopes with soft β -radiation (^{35}S , ^{45}Ca , ^{14}C) and to work with adsorbate concentration generally not exceeding $10^{-3} M$. The fact is that at high adsorbate concentrations and with hard β or γ radiation, the solution "background" (I_p) rises sharply as compared to I_a . At lower adsorbate concentrations it is sometimes possible to carry out measurements with isotopes emitting intermediate or hard β radiation.⁽⁷⁷⁾

The preparation of electrodes with reproducible adsorption properties and the replacement of electrodes present certain difficulties. The use of gold foil is accounted for by the fact that owing to its high plasticity, gold alone can be rolled to $\sim 1 \mu\text{k}$ without formation of holes or cracks in the foil. The choice of gold as metal for metallization of polymer films is dictated, on one hand, by its chemical inertness and, on the other hand, by the fact that the gold sputtering process is well known and can be easily carried out. However, it should be borne in mind that no special study has been made of the influence of a gold substrate on the adsorption properties of platinum electrolytically deposited on it. In the general case, this influence does not seem to be large because the results of the measurements on platinized platinum by electrochemical methods and on platinized gold by the "foil" method are in good agreement (Figure 10).⁽⁷⁸⁾

The most important scientific result achieved by the "foil" techniques is the establishment of the main features of the adsorption of organic compounds on catalytically active metals.^(72,78)

Quite recently Gorodetski and co-workers⁽⁷⁹⁾ proposed a new radioactive tracer technique for investigation of the adsorption, desorption, and exchange of pre-adsorbed particles. Essentially, this technique combines two methods: the "solution" method with adsorbate circulation and the "foil" method, thus, in principle, allowing the increase of the amount of adsorbate on the electrode and its decrease in solution to be followed simultaneously. This doubling of the parameters being measured enhances significantly the reliability of the obtained experimental data. The schematic of the equipment is shown in Figure 11. The main features of this equipment are as follows. The solution in the cell is well stirred, moving along a closed circuit. The circulation is effected by means of two magnetic stirrers. The design of the cell allows for a quick substitution ($\sim 1 \text{ s}$) of the radioactive solution in the cell by the same solution, but nonradioactive, which is very important in studying the exchange processes of pre-adsorbed substance. The advantages, disadvantages, and

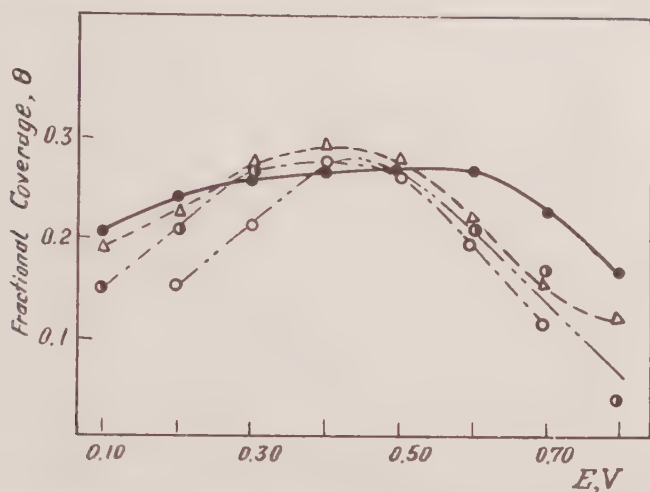


Figure 10. Dependences of the extent of adsorption of benzene on the potential of a platinum electrode obtained by different methods: ● tracer method, $C_{C_6H_6} = 1.1 \mu M$; Δ pulse method, $C_{C_6H_6} = 1.4 \mu M$; $\circ$ potentiostatic method, $C_{C_6H_6} = 1.1 \mu M$; $\bullet$ galvanostatic method, $C_{C_6H_6} = 1.3 \mu M$.⁽⁷⁸⁾

possibilities peculiar to the “solution” and “foil” methods hold true for this technique as well. Its additional limitations are, first, the adsorption kinetics generally cannot be measured simultaneously from the radioactivity decrease in the solution and increase on the electrode; second, the extent of adsorption can be determined from the radioactivity of the electrode only after removing the adsorbate solution from it, by washing. For this reason it is not possible to take account of that part of the adsorbed substance removed by washing. Nor can this be done by extrapolation of the dependence of the radioactivity of the substance adsorbed on the electrode on the washing time to zero washing time since the washing is performed in a crude way. The technique under consideration was used for investigation of the adsorption of iodine ions on a bismuth electrode at adsorbate concentrations in solution of 2×10^{-9} – 3×10^{-4} M. The technique proposed in Reference 79 offers some advantages in studies of fast desorption and exchange processes, and of adsorption processes at adsorbate concentrations $\leq 10^{-4}$ M.

2.3.2. The “Thin Layer” Method

The necessity to use isotopes with soft β -radiation reduces sharply the number of substances whose adsorption can be studied by the “foil” method. The number of isotopes suitable as labels could be increased with the use of a specially designed cell (Figure 12), proposed by Kafalas and Gatos.⁽⁸⁰⁾ A very thin solution layer (~ 0.5 mm) flows over the electrode in the form of a plate. The radiation counter is placed on the solution side, which makes it

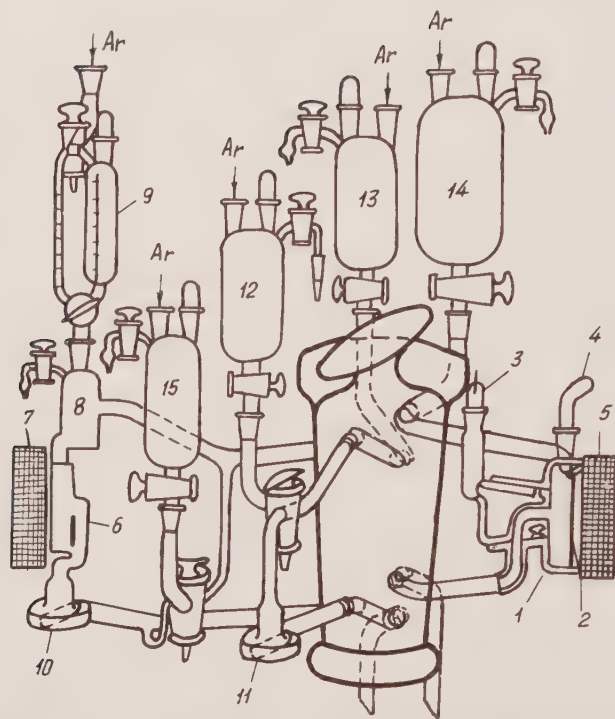


Figure 11. Design of the measuring cell: (1) cell body, (2) working electrode, (3) auxiliary electrode, (4) salt bridge, (5), (7) detectors, (6) measuring volume, (8) buffer volume, (9) burette, (10), (11) stirrers, (12), (13), (14), (15) vessels for preparation of solution.⁽⁷⁹⁾

possible to reduce the radiation absorption, as compared to the "foil" method. The cell wall facing the counter is usually made of mica. The techniques based on this principle belong to the subgroup of "thin layer" methods.

The number of studies carried out by means of the "thin layer" method is not large. It was used to study anion adsorption on zirconium, copper, nickel,^(81,82) platinum,⁽⁸³⁾ and germanium.⁽⁸⁴⁾

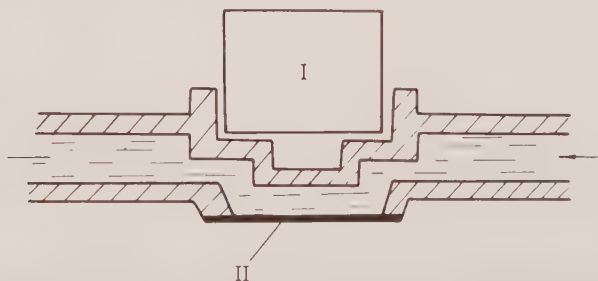


Figure 12. Cell for adsorption measurement by the "thin layer" method: (I) radiation counter, (II) metal specimen (working electrode).⁽⁸⁰⁾

An advantage of this method is the possibility of performing measurements on smooth metals at small concentrations.

The main drawbacks of the method are: the complexity of the equipment, incorporating a pump for solution circulation, the difficulty of measuring potential and electrode polarization, and the difficulty of ensuring high purity in the experiment. Owing to its insufficient sensitivity, the method can be used only for investigating the adsorption of strongly surface-active substances, interacting chemically with the adsorbent.

Due to the radiation absorption in the solution layer, the method is not applicable to adsorption measurements of compounds labeled with an isotope emitting soft β -radiation.

Recently Titkin⁽⁸⁵⁾ suggested a version of the "thin layer" method which differs from those described above in that the thickness of the flowing solution layer can be controlled by means of a micro-screw.

The general scheme of the set-up is shown in Figure 13. All vessels and connecting tubes are made from Teflon or Pyrex. The body of the measuring cell is made from Teflon. In the center of the body there is a cylindrical hole inside which a Teflon piston, with the electrode built into it, moves. Over the rear end of the cell turned towards the counter, a synthetic film is stretched. The pump is all Teflon.

The new version was tested in the determination of the dependence of the extent of adsorption of iodine ions on the potential of smooth platinum and showed good agreement of the results with similar data obtained earlier by other radiochemical methods.

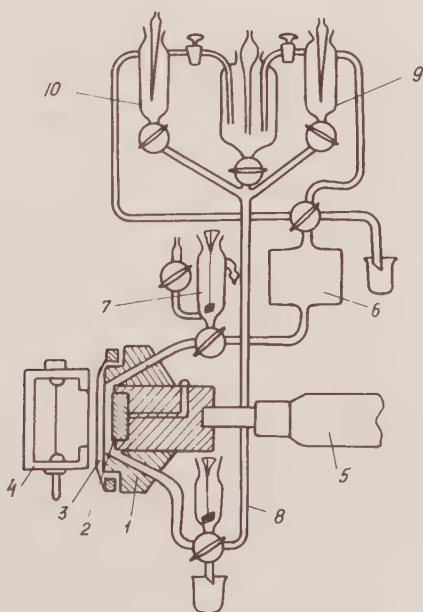


Figure 13. Cell for Adsorption measurement by the "thin layer" method: (1) Teflon cell body, (2) metal specimen, (3) membrane, (4) radiation counter, (5) micrometric screw for moving the electrode, (6) pump, (7) reference electrode, (8) polarization electrode, (9), (10) vessels for preparation of solution.⁽⁸⁵⁾

2.3.3. The "Electrode Lowering" Method

The method described below was proposed by Kazarinov in 1966⁽⁸⁶⁾ for investigation of the adsorption on electrodes with a highly developed surface. Later he developed and refined this method,^(87,88) which made it possible to apply it to adsorption studies on smooth metals.

Basically, the method consists of the following. For measuring the radioactivity of the substance adsorbed on the electrode, the electrode in the form of a disc is lowered to the bottom of an electrochemical cell for which a thin membrane is used. The radioactivity measured by the counter when the electrode is immersed (I_u) is made up of the following quantities: the radioactivity of the adsorbed substance (I_a), the radioactivity of the thin solution layer between electrode and membrane (I_K), the radioactivity of the labeled substance adsorbed on the membrane (I_M), and the radioactivity resulting from radiation from the solution bulk (I_p). Thus $I_u = I_a + I_K + I_M + I_p$. Hence it follows that $I_a = I_u - (I_K + I_M + I_p)$. It is clear that the systematic error is less, the lower the sum of the quantities in brackets. To increase the accuracy of determination of I_a the quantities I_M , I_K , and I_p must be reduced to a minimum.

The quantity I_M depends on the adsorbate nature and membrane material and can be readily determined in each particular case. For this purpose, for instance, it is necessary to measure the radioactivity of the cell (without the electrode) with the solution being tested and with the solution of the same specific radioactivity (pulse/min mL) as the test solution but with a much higher adsorbate concentration. The difference in these quantities is I_M .

The membranes must satisfy the following requirements:

1. they must be sufficiently thin, so that they adsorb the isotope radiation only slightly;
2. they must be mechanically strong, so that they withstand the pressure of the solution and the electrode weight and the excess pressure of the gases in the cell;
3. they must be chemically stable in the media being investigated;
4. they must not change their physical properties during prolonged experiments, e.g., they must not swell;
5. they must not adsorb and absorb labeled adsorbate in appreciable amounts.

After testing a large number of polymer films (mica, Teflon, terylene, polyethylene, etc.), terylene (polyethylene terephthalate) was chosen. This polymer is a product of the re-esterification of dimethyl terephthalate with ethylene glycol in the presence of catalysts, followed by polycondensation of the product diethylol terephthalate. Polyethylene terephthalate is insoluble in ordinary organic solvents and therefore films from this polymer are made only from a melt with subsequent stretching and heat treatment.

A polyethylene terephthalate film has the following physico-mechanical properties⁽⁸⁹⁾:

Melting point 250°C ;
Tensile strength $1000\text{--}1800\text{ kg/cm}^2$;
Surface resistivity 10^{12} cm ;
Density 1.38 g/cm^3 ;
Flexing resistance (number of cycles) $20,000$;
Dielectric constant at 60 cps $3.1\text{--}3.2$.

Such films $5\mu\text{k}$ thick ($\sim 0.7\text{ mg/cm}^2$) possess a sufficient mechanical strength, are continuous, and at the same time, due to their high crystallinity ($\sim 80\%$), do not swell in aqueous solutions. As shown by experiment, the films are chemically stable for several weeks in the inorganic systems studied in the pH range $0\text{--}14$ and also in the presence of organic substances. Only in the presence of labeled acetate ions does the radioactivity of the films slowly increase, apparently due to chemical interaction. Terylene films adsorb ions and molecules in insignificant amounts. Washing the membrane with several portions of water after it has been in contact with labeled adsorbate for a long time decreases its radioactivity almost to zero. Addition of a stable adsorbate excess to the labeled adsorbate contained in the cell does not change the radioactivity being measured. The behavior of the membrane during the experiment is controlled by measuring the solution radioactivity. A constant radioactivity value indicates that there is no mechanical damage and the other conditions of measurement are unchanged (it being understood that the adsorbate concentration in solution does not change). It should be noted that an increased radioactivity after removal of labeled adsorbate and washing of the cell does not always indicate adsorption on the membrane. More often it is caused by adsorption on glass (especially on ground glass), penetration of solution into spots inaccessible to washing, or by some other similar factors.

Some techniques have been developed for mounting the membrane. First the film is fitted between polystyrene rings by means of screws and then, by special union nuts, it is stretched either over the counter or the cell body.

At the lower electrode position the value of I_p corresponds to the intensity of the radiation passing through the electrode and also through the walls of the cell and the counter from the solution bulk. When electrodes 3 mm thick and shields with a protective lead layer about 5 mm thick are used, the β -radiation can be considered to be completely adsorbed. In this position the counter registers γ -radiation (both primary and breaking). The fact that platinum has a large specific gravity favors complete absorption, which, by the way, affects adversely the measurements by the "foil" method as it decreases sharply the radiation registration efficiency.

The quantity I_K is the largest in the sum of the quantities in brackets. The thickness of the solution layer between membrane and electrode depends on the ideal state of the membrane and electrode planes. For better fitting of the membrane, the plane of the counter body over which it is stretched is precision-polished. The rear end of the cell with the wall thickness of $\sim 3\text{ mm}$ is also polished. This prevents leaking of the solution after the cell and the

counter are connected. In the case of smooth polished electrodes, the thickness of the solution layer between membrane and electrode is no more than 0.01 mm. This was found by comparing the radioactivity of the solution labeled with ^{35}S with that measured at the lower electrode position when the adsorption on it is zero (this condition is realized at a reversible hydrogen potential).

The radiation intensity of the solution is determined by the expression:

$$I_p = \lambda c \int_0^\infty e^{-\mu x} dx = \lambda \frac{c}{\mu} \quad (11)$$

where $\lambda = A I^0 \beta$, β is the counting efficiency, A is the geometric surface of the electrode, I^0 is the specific radioactivity of the solution, μ is the absorption coefficient ($\text{cm}^2 \text{mg}^{-1}$), and x is equivalent to the distance between membrane and electrode.

In the case of the lower electrode position we have:

$$I'_p = \lambda c \int_0^l e^{-\mu x} dx \quad (12)$$

With I_p and I'_p known from experiment, we can easily calculate l .

In the case of platinized platinum this layer reaches 0.03 mm. Sometimes when electrodes undergo platinization, dendrites up to 1 mm in size grow on their surface. Naturally, in their presence, measurements with the use of isotopes emitting soft β -radiation are impossible. Therefore, after platinization, it is necessary to remove all macroroughnesses by laying the electrode over a polished glass and moving it along the latter.

For determining I_a there is no need to measure separately I_M , I_K , and I_p . It is sufficient to know the sum of these quantities and to ensure that they remain constant during the experiment. This can be readily achieved by measuring the radioactivity in the upper electrode position. The sum ($I_M + I_K + I_p$) can be determined in several ways, just as in the "foil" method. One of them involves measuring the radioactivity in the lower electrode position in the absence on the electrode of labeled substance in the adsorbed state. These conditions can be found from independent measurements or produced artificially by significant ($\sim \times 100$) increase of the unlabeled adsorbate concentration. In the latter case the contribution of the radioactive adsorbate to adsorption is less than 1% and can be neglected. The sum ($I_M + I_K + I_p$) can be determined also by measuring the radioactivity at the lower electrode position in the solution containing some other substance labeled with the same isotope but not adsorbed on the electrode. In this case the specific radioactivities (pulse/min mL) of the two solutions must be the same.

The absolute values of the extent of adsorption are determined by comparing the values of I_a with the radioactivity of a known amount of given substance deposited on the same electrode. To determine the absolute amounts of organic substance adsorbed on platinum, Kazarinov and co-workers⁽⁹⁰⁻⁹²⁾ suggested

a technique based on the use of methanol as a standard. The technique is basically as follows. After measuring the charging curve on the electrode at $E_r^\dagger = 0.5$ V, labeled methanol is adsorbed from 0.1 M $\text{CH}_3\text{OH} + 0.5$ M H_2SO_4 solution. Then the radioactivity of the adsorbed substance is measured and it is subjected to electro-oxidation in the adsorbed layer. It can be considered to be definitely established⁽⁹³⁾ that under these conditions the amount of adsorbed particles containing one carbon atom is 3.4×10^{14} particles/cm² true surface. Then another substance is adsorbed on the same electrode and its radioactivity is measured. If we know the specific radioactivity of methanol and of the substance being investigated and their radioactivity in the adsorbed state, we can determine the extent of adsorption sought:

$$N_x = 3.4 \times 10^{14} \frac{I_x \cdot I_{\text{CH}_3\text{OH}}^S}{I_{\text{CH}_3\text{OH}} \cdot I_x^S} \quad (13)$$

In our opinion, this technique is the simplest and the most reliable since, in the determination of the extent of adsorption, the adsorption capacity of the surface with respect to hydrogen and methanol is controlled (the length of the section of the charging curve corresponding to methanol electro-oxidation should be ~ 0.8 of the length of the hydrogen section of the charging curve in 1 N H_2SO_4).

The sensitivity and accuracy of the technique depend on the relation between I_u and I_a and can be estimated in the usual way in each particular case. The sensitivity of the technique depends directly on I_K since I_a is determined as an excess over I_K . Thus, it is clear that for determination of I_a to within $\pm 50\%$, the value of I_a should not be less than the doubled mean error of measurement of I_K . Since I_K varies in direct proportion to the labeled adsorbate concentration in solution and I_a usually increases in proportion to the logarithm of the concentration, then at a certain concentration, the adsorption effect (I_a) becomes commensurable with I_K or less than I_K . Conditionally this concentration can be considered to be the upper limit of concentrations accessible to adsorption measurements. Naturally, this limit depends on the adsorbability of the substance and the true electrode surface. As shown by experiment, reliable results can be obtained up to a concentration of 10^{-1} M. It can be seen from the expression for I_a that enhancement of the sensitivity of the technique would involve decreasing the thickness of the solution layer between membrane and electrode since, on one hand, this increases the registration efficiency of the adsorbed substance radiation and, on the other hand, decreases I_K .

The choice of cell design and of counting equipment is defined by the objects of the investigation. The technique under consideration can be applied in measurements with isotopes emitting any kind of radiation and can be used in conjunction with different radiation counters.

$\dagger E_r$ is the electrode potential against a reversible hydrogen electrode in the same solution.

Some types of cells used in the "electrode lowering" method are shown in Figures 14 and 15.

The electrode is moved in the vertical direction by means of a cylindrical ground glass joint or by hydraulic gate. The cylindrical ground glass joint can be easily made from a standard 2-ml hypodermic syringe by substituting the bushing by a ground glass tube. The vessels for preliminary preparation of solutions allow for saturation with necessary gases or vapors of organic substances. The design of the vessel for preliminary preparation of solution is given in Figure 14. Its use can solve practically all problems arising in the course of an electrochemical experiment. In particular, it is possible to prepare

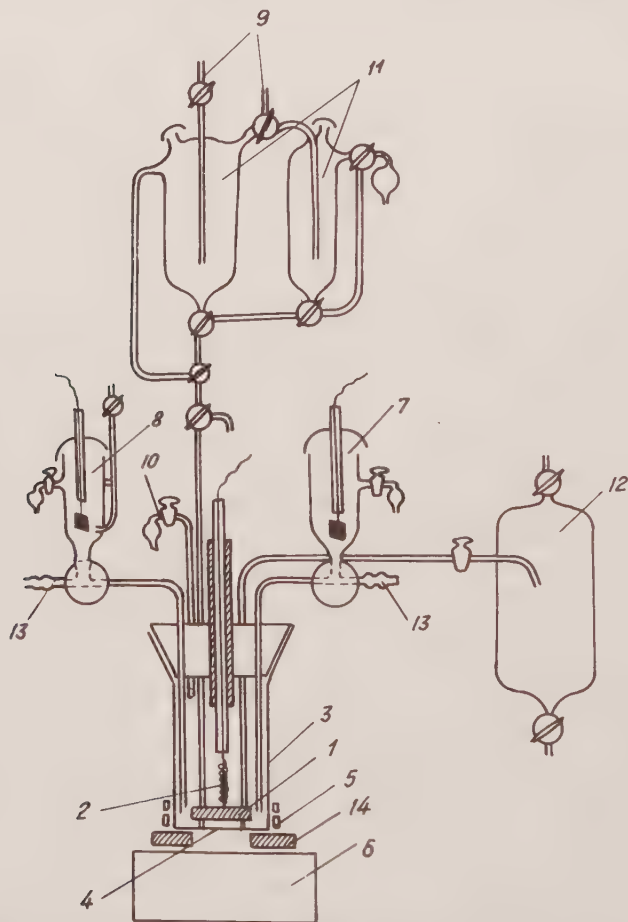


Figure 14. Cell for adsorption measurement by the "electrode lowering" method: (1) working electrode, (2) flexible contact, (3) cell body, (4) membrane, (5) membrane mounting, (6) radiation counter, (7) auxiliary electrode, (8) reference electrode, (9) gas inlet, (10) gas outlet, (11) vessel for preparation of the solution, (12) solution sink, (13) connecting tubes, and (14) shielding.⁽⁸⁶⁾

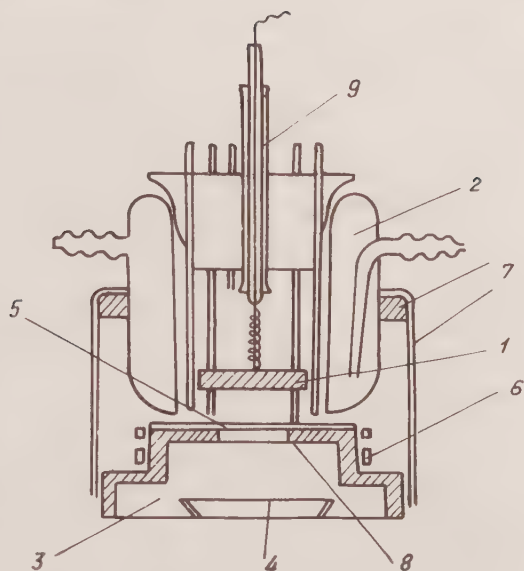


Figure 15. Adsorption measurement by the "electrode lowering" method: (1) working electrode, (2) jacket for thermostatic control, (3) radiation counter, (4) counter filament, (5) membrane, (6) membrane mounting, (7) fixation of the cell to the counter, (8) counter window, (9) cylindrical ground glass joint.⁽⁸⁷⁾

simultaneously the solution of organic substance and the solution for washing the main cell.

The solution is removed from the main cell either by producing in it, by means of an inert gas, some excess pressure, under the action of which the solution is pressed into the collecting vessel, or by producing a partial vacuum in this vessel with the use of a syringe. The electrode potential is measured in the conventional manner. Some designs allow for the possibility of turning the tip of a Luggin capillary in such a way that it approaches directly the underside of the electrode. The design of the cell shown in Figure 15 allows for operation under thermostatic control.

Under the reference and the auxiliary electrodes there are special bulbs which enable washing of the electrodes without changing the solutions. This is effected by producing a vacuum in the bulbs by means of a syringe, whereupon the solution is poured off. In most cell designs, by means of interchangeable ground glass joints the polarization electrode can be located in the same compartment as the operating electrode or in a separate compartment.

When working with isotopes emitting soft β -radiation (^{45}Ca , ^{14}C , ^{35}S), it is advisable to use a flowing-gas counter which has a higher efficiency. The counting efficiency can be increased further by using scintillation counters, especially liquid ones. But this complicates the technique of measurement. When working with isotopes with mixed β - and γ -radiation, it is convenient to use the usual commercially available counters (MST-17, Si-2BG, etc.).

When working with electrodes from smooth metals, special measures are taken to enhance the sensitivity. The electrode surface is mechanically polished. The volume of the adsorbate solution is reduced to 1–2 mL. The diameter of

the cell body exceeds that of the electrode by only 2 mm. Since it is essential to keep the potential constant during the experiment when working with smooth electrodes, in order to prevent breaking of the contact in the electric circuit when the electrode is in the lower position, a thin platinum spring is used connecting the "leg" of the electrode and the platinum hook soldered in the piston of the cylindrical ground glass joint.

The advantages of the "electrode lowering" method are as follows. The measurements can be performed without interrupting the adsorption process (just as in the "foil" method). An isotope with any kind of radiation can be used as a label. The measurements can be carried out both on smooth (compact) metals and on metals with a highly developed surface. The method allows adsorption radioactive tracer measurements to be combined with galvanostatic and potentiostatic measurements in the case of an electrode with a highly developed surface. Such measurements would be impossible with any other methods. For example, in the case of the "foil" method it was necessary to increase the roughness in order to perform reliable electrochemical measurements, but increased platinization led to decrease of the counting efficiency.

The limitation of the method is that it cannot be used at potentials at which large currents flow in the circuit and vigorous gas evolution is observed.

The "electrode lowering" method can be used to study at different potentials the adsorption and desorption kinetics as well as the kinetics of exchange of pre-adsorbed substances with the same substances in solution. From these data the rate constants of adsorption, desorption, and exchange are calculated. Figure 16 shows the characteristic data on the exchange kinetics at different potentials.

The method under consideration permits the measurement of the dependences of the extent of adsorption on the temperature, electrode potential,

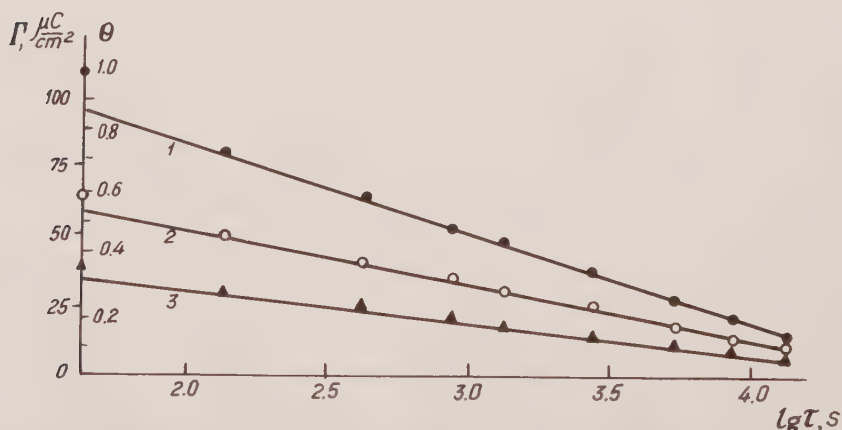


Figure 16. Dependence of the amount of thallium ions remaining in the adsorbed state on the logarithm of the exchange time at different potentials: (1) 0.0 V, (2), 0.4 V, (3) 0.8 V.⁽¹⁰⁰⁾

and adsorbate concentration in solution in different ways, as illustrated by the data in Figure 17. From the data on the dependence of adsorption on temperature, the activation energy of adsorption is calculated.

The method affords information on the electric double layer structure, in particular, on the location of the potential of the conditional zero charge and the influence on it of surfactants (Figure 18), and also on the influence of organic and inorganic substances on mutual adsorption (Figure 19).

By combining the measurements by the "electrode lowering" method with electrochemical measurements in adsorption studies of organic substances, it is possible to have information on the mechanisms of adsorption and of oxidation of an adsorbed particle as well as on its stoichiometric composition. For determination of the stoichiometric composition, Kazarinov and co-workers⁽⁹³⁾ proposed a procedure of determining the mean number of electrons (n_e) participating in the oxidation of a chemisorbed particle with one carbon atom. The procedure is as follows. Under preset conditions, organic substance labeled with ^{14}C is adsorbed on the electrode. Then, simultaneously with the electro-oxidation of the chemisorbed substance, the dependence of the amount of carbon-containing particles remaining on the electrode (N) on the quantity

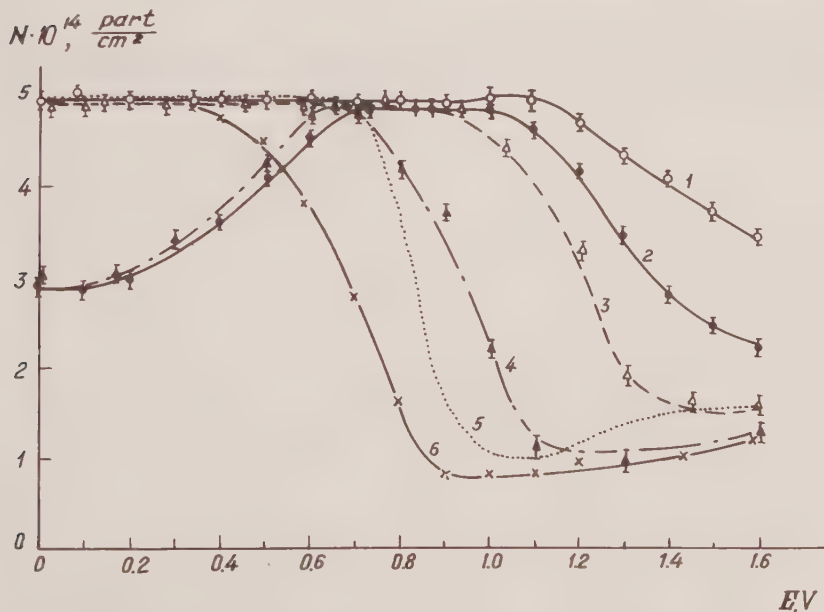


Figure 17. Dependence of the extent of adsorption of thiourea labeled with the isotope ^{14}C (Curves 1, 3, 5) and with the isotope ^{35}S (Curves 2, 4, 6) on the potential of smooth platinum in a $10^{-3} \text{ M } (\text{NH}_2)_2\text{CS} + 1 \text{ N H}_2\text{SO}_4$ solution. The potential was varied from 0.0 to 1.6 V (Curves 1, 2) and from 1.6 to 0.0 V (Curves 5, 6). Curves 3 and 4 are plotted from the limiting values of the kinetics adsorption isotherms at each potential.⁽⁹²⁾

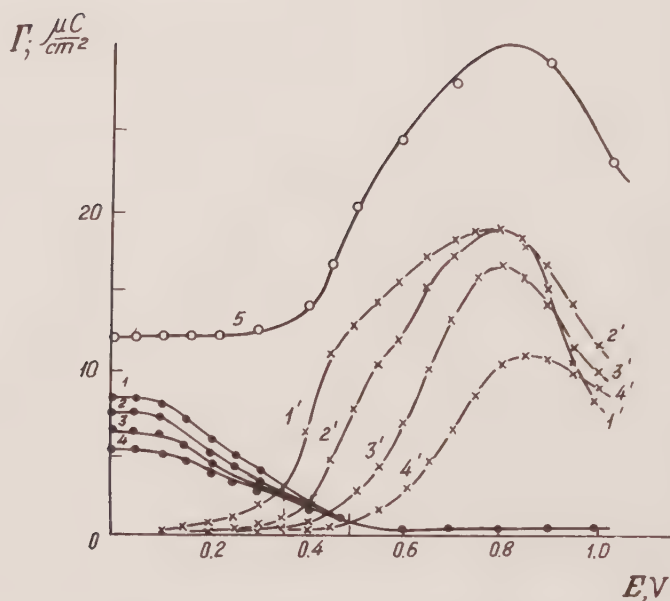


Figure 18. Dependence of the extent of adsorption of Na^+ cations (Curves 1–4) and HSO_4^- anions (Curves 1'–4') on the potential of platinized platinum in a $3 \times 10^{-2} N \text{ NaSO}_4 + 10^{-2} N \text{ H}_2\text{SO}_4$ solution, with iodine ion adsorption equal to: 0 (1), (1'), 0, (2), (2') 12, (3), (3') 26, (4), (4') $38 \mu\text{C}/\text{cm}^2$. Curve 5 is the dependence of the adsorption of $\Gamma_{\text{HSO}_4^-} + \Gamma_{\text{I}^-}$ on E for iodine adsorption $\Gamma_{\text{I}^-} = 12 \mu\text{C}/\text{cm}^2$.⁽⁹⁸⁾

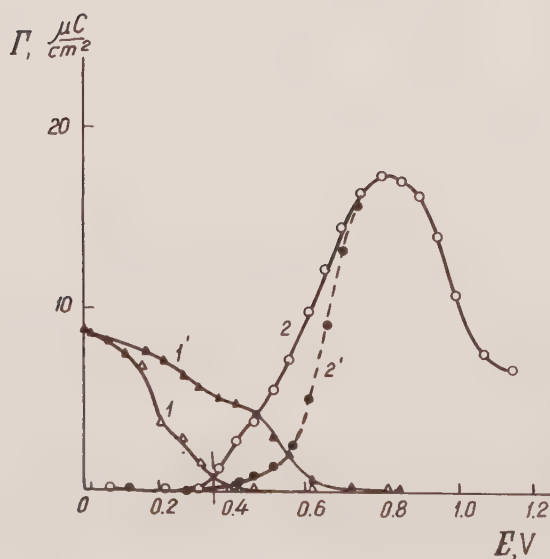


Figure 19. Dependence of the adsorption of ions on the potential of a Pt/Pt electrode in a $10^{-3} N \text{ H}_2\text{SO}_4 + 3 \times 10^{-3} N \text{ Na}_2\text{SO}_4$ solution: (1) Na^+ and (2) HSO_4^- on the surface free of methanol; (1') Na^+ and (2') HSO_4^- in the presence of chemisorbed methanol.⁽¹¹³⁾

of the electricity passed (Q) is measured. From the slope of the straight line of the N - Q plot the quantity $\Delta Q/\Delta N$ is calculated, the numerical value of which corresponds to the value of n_e .

In a steady-state oxidation process of an organic substance, it is possible to determine the oxidation kinetics of the pre-adsorbed organic substance and from these data a conclusion can be drawn about the electro-oxidation mechanism. The relevant data for the electro-oxidation of methanol on a Pt/Pt electrode are given in Figure 20.

The "electrode lowering" method can be used successfully with differential and kinetic isotopic methods in the adsorbate-adsorbent systems to obtain information on the energetic structure of the adsorbent surface and to study the influence of trace amounts of poison on the adsorption of hydrogen, oxygen, and organic and inorganic substances on solid electrodes.

The data obtained by the described method are completely reproducible within the experimental error, which even under the most unfavorable experimental conditions is no higher than $\pm 5\%$.

The high reproducibility of the data is illustrated in Figures 21,⁽⁹⁴⁾ 22,⁽⁹⁵⁾ and 23.⁽⁹⁰⁾ It can be seen that the data agree well with the those obtained by other methods.

Among the important scientific results obtained by the "electrode lowering" method are information on the electric double layer structure on platinum,⁽⁹⁶⁻⁹⁸⁾ and data on ion adsorption on platinum group metals,⁽⁹⁹⁻¹⁰²⁾ on the adsorption of organic substances on platinum⁽¹⁰³⁻¹⁰⁹⁾ and their influence on ion adsorption,⁽¹¹⁰⁻¹¹³⁾ and on the surface inhomogeneity of platinum.⁽¹¹⁴⁻¹¹⁵⁾

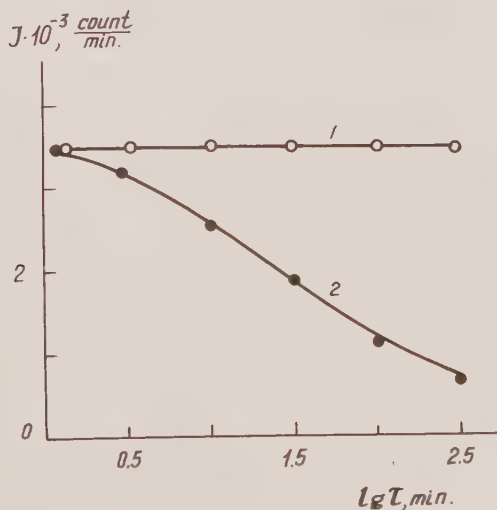


Figure 20. Change in the radioactivity of labeled chemisorbed methanol upon contact with stable methanol solution ($0.1 M \text{CH}_3\text{OH} + 0.1 M \text{H}_2\text{SO}_4$) in the absence (Curve 1) and presence of polarization (Curve 2).⁽¹¹⁰⁾

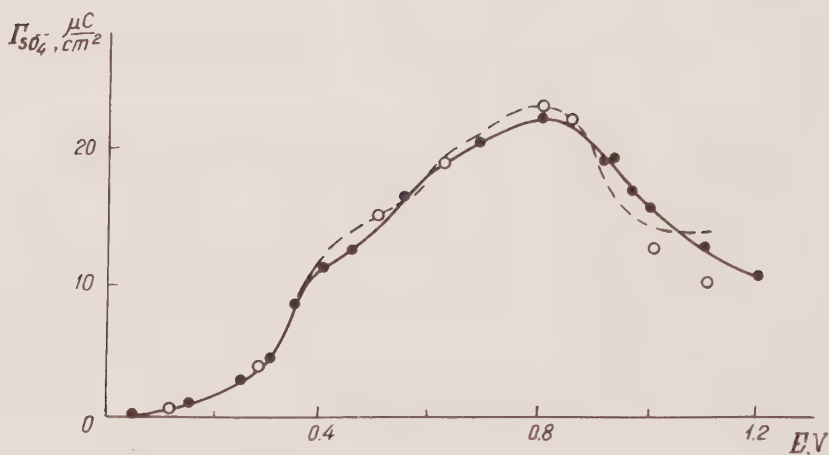


Figure 21. Dependence of the extent of adsorption of sulfuric acid anions in $10^{-2} N H_2SO_4$ solution on the potential of a Pt/Pt electrode obtained by different methods: ●— measured by the tracer method, ○ measured by titration, — — — calculated from the isoelectric potential shifts and the charging curve.

3. Radioactive Tracer Methods Used for Investigation of the Dissolution Processes of Metals and Alloys

In the radioactive tracer methods for investigation of the dissolution of metals or alloys, radioisotopes of the metal or of the elements constituting the metal alloy are introduced into the test specimen; then the specimen is

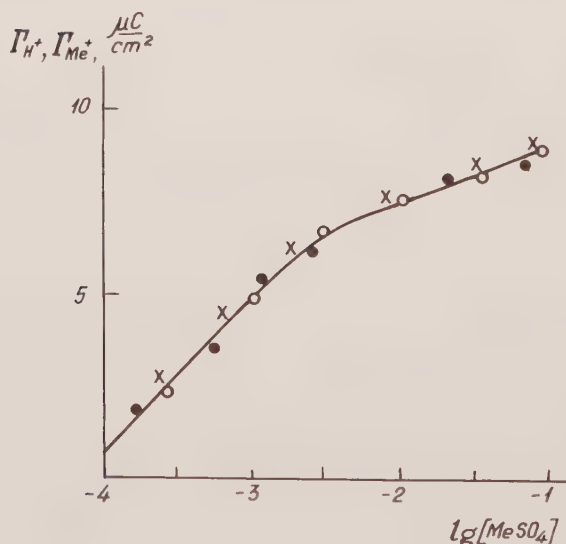
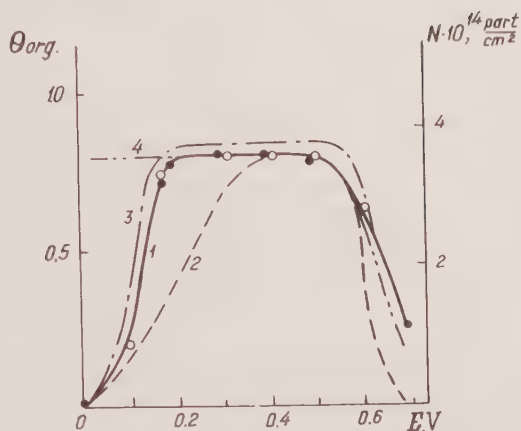


Figure 22. Dependences of the quantities Γ_{H^+} and Γ_{Na^+} on the logarithm of salt concentration; $pH = 3$, $\varphi_r = 0.0 V$. × data obtained by the radioactive tracer method, ○ data obtained by titration.

Figure 23. Dependences of the extent of adsorption (surface coverage) of methanol on the potential of a platinum electrode from the data of measurements by the radioactive tracer method (Curve 1⁽⁹⁰⁾) and from the data of electrochemical measurements (Curves 2,⁽¹⁷⁴⁾ 3,⁽¹⁷⁷⁾ 4⁽¹⁷⁶⁾).



subjected to special electrochemical treatment during which it undergoes dissolution. The dissolution rate of the specimen is assessed from the rate at which the radioisotope passes into solution, which can be determined both from the increase of the amount of radioisotope in solution and from its decrease on the specimen electrode. On this principle, all radioactive tracer methods used for investigation of dissolution processes can be divided into two groups.

The application of the radioactive tracer methods to investigation of dissolution processes is possible only if the following conditions are satisfied. First, it is necessary that the radioisotope should be uniformly distributed both in the test specimen and in the solution into which it has passed during the dissolution process. Naturally, this means that the dissolution products must be soluble. Second, characteristics of the isotopes used (kind and energy of radiation, half-life) should be appropriate to the conditions and duration of the electrochemical treatment.

Both these conditions are directly related to the mode of introduction of the radioisotope into the specimen. If the dissolution of metal amalgams is studied, the radioisotope is introduced into the amalgam during its preparation, which ensures a uniform distribution of the radioisotope in the amalgam. This, in its turn, makes amalgams a very convenient object of investigation.⁽¹¹⁶⁻¹³¹⁾

In the case of solid electrodes the radioisotope can be introduced into the specimen in three ways: (1) it can be introduced into a metal melt from which the electrode is prepared after solidification of the melt; (2) radioactive metal is deposited by a galvanic process on a nonradioactive substrate from the same metal; or (3) the metal specimen is subjected to neutron irradiation in a nuclear reactor.

Just as in the case of amalgams, introduction of the radioisotope by the first method ensures its uniform distribution in the specimen and permits its use as soon as it is prepared.

The second method of radioisotope introduction has the advantage that at a high surface radioactivity of the specimen, its total specific radioactivity remains comparatively low, which is favorable for recording the dissolution rate; it allows the specimen to be used as soon as it is prepared. Among the disadvantages of the second method are: the difficulty of preparing electrolytic coatings which do not crumble during electrochemical treatment and are of the same thickness over the whole area of the specimen; the necessity to increase the thickness of the coatings in order that the isotope content (concentration) in the surface layers of the specimen be the same at all points and change in the course of the dissolution process only as the result of isotope decay but not due to diffusion of the substrate atoms. Moreover, the results of the measurements of the dissolution of electrolytic coatings cannot be fully extended to compact metals, which decreases significantly their value. The information on the use of this method available in the literature refers mainly to platinum group metals.^(41,132)

The third method of isotope introduction is thermal neutron flux irradiation of the specimen in a nuclear reactor. The interaction of neutrons with a natural mixture of stable isotopes of a given element yields its radioisotopes. This method can be used when the radioisotopes formed during irradiation have suitable characteristics: kind and energy of radiation, specific radioactivity, half-life. The advantages of this method are the simplicity of the isotope introduction and its uniform distribution in the specimen. The latter factor makes it possible to conduct electrochemical experiments during a long period of time without risk of a change in the ratio between radioactive and stable isotopes in the surface layer and in the specimen bulk.

However, this method has some serious drawbacks.⁽¹³³⁾ The first of these is the possibility of errors associated with the presence in the specimen of surface and bulk micro-impurities. If the micro-impurities have a large activation cross section and are strongly activated upon neutron irradiation, then when they pass into solution together with the base metal during electrochemical treatment, they can make an essential and even decisive contribution to the total radioactivity. In view of this fact, a radiochemical analysis of the solution samples by measuring the total radioactivity using ordinary radiometric equipment may lead to erroneous results.⁽¹³⁴⁾ It is possible to avoid this difficulty by measuring the radiation spectra by means of scintillation gamma-spectrometers. By using spectrometers, it is possible to separate from the total radiation spectrum the lines of particular radioisotopes and after their measurement to calculate from the intensity (if calibration data are available) the content of the corresponding elements in the sample. This method of radiochemical analysis was proposed by the Japanese scientists Mituya and Obayashi^(135,136) and was further substantially improved at the Karpov Institute of Physical Chemistry in Moscow.⁽¹³⁷⁻¹⁴⁰⁾

The use of scintillation gamma-spectrometers instead of ordinary total radioactivity counters not only eliminates the influence of microimpurities on

the results of measurements, but also has other advantages. First, the sensitivity of the method is significantly enhanced due to increase in the registration efficiency of gamma-pulses and a better ratio of useful signal to background, since it is only the part of the background corresponding to the radiation energy in the photopeak region of the radioisotope of interest which is taken account of. Second, if the test specimen is an alloy, then it is possible in principle to determine not only the overall but also the partial dissolution rates of the alloy components. In working with a single-channel scintillation spectrometer without radiochemical separation, 3-4 elements can be determined in the sample while with the use of multichannel spectrometers up to 6 elements can be determined.⁽¹³³⁾

At the same time, it should be pointed out that the use of spectrometers involves some complications: the need for special sample preparation before analysis, the considerable amount of time involved, and the difficulty of interpretation of gamma-spectra. These complications preclude working with short-lived isotopes and studying fast dissolution processes (<a few minutes).

The second serious drawback of isotope introduction into the specimen by irradiation in a nuclear reactor is the presence of radiation effects. Two kinds of such effects are possible. The first of these is that under the influence of neutron and gamma radiations of the reactor, some changes can occur in the structure and composition of the specimen, caused by the appearance of vacancies and incorporation of atoms into the interstices of the metal lattice and by formation of impurity element atoms as the result of nuclear reactions. This can lead to a change in the surface properties of the specimen.

The effects of this kind increase with the irradiation time, but their action can be weakened by heating the specimen and by its treatment in concentrated acids at elevated temperatures.⁽¹³⁷⁾

The effects of the second kind are as follows. When a radioactive specimen is placed into solution, the composition of the layer adjacent to the electrode can change due to appearance of radicals and other radiolysis products. The interaction of these products with the specimen surface may affect its dissolution process.⁽¹⁴¹⁾ These effects depend on the specific radioactivity of the specimen and decrease as it decays with time. For this reason, it is necessary to hold the specimen for some time after irradiation ("cooling") before the beginning of the experiment. It follows from literature data⁽¹⁴²⁻¹⁴⁷⁾ that all radiation effects can influence appreciably the dissolution processes of metals and alloys, and therefore it is imperative that they should be taken into account and assessed in each particular case.

The specific features of radioisotope introduction into the specimen by irradiation in a nuclear reactor define the type of dissolution processes for which this method has found wide use. These are the dissolution processes of corrosion-resistant metals and alloys.^(137-140,148-151)

Having defined the conditions for applicability of radioactive tracer methods and having considered the main features of radioisotope introduction

into the specimen, we shall examine in detail each of the two groups of radioisotope techniques used for investigation of dissolution processes.

3.1. Methods Based on the Determination of the Radioisotope Concentration in Electrolyte Solution

The simplest technique for determination of dissolution rate with the use of a radioactive tracer (radioisotope) introduced into the specimen (electrode) is electrolyte sampling at regular intervals ("sampling" method), the radioactivity of the samples being measured by radiometric or spectrometric equipment. Sampling can be carried out with or without interruption of the electrochemical process. When using this method the choice of the radioisotope tracer, the technique of treatment of samples before analysis, and the method of analysis itself do not depend on the experimental conditions. This means that it is possible to use practically any γ and β isotopes, ensuring a relatively high sensitivity, and, in principle, to determine the partial dissolution rates of alloy components. The absolute amounts of the electrode substance dissolved in a given time are determined from radiochemical analysis of solution samples, with the specific radioactivity of the electrode material known.

This technique was used for investigation of the exchange currents of bismuth, zinc, and lead amalgams with solutions of their salts.⁽¹¹⁶⁻¹²⁰⁾ Pleskov and Miller⁽¹¹⁹⁻¹²⁰⁾ proposed a method for calculation of the exchange currents on the basis of the time dependence of solution radioactivity. A relative error in the experimental data obtained was 15-20%. Such high relative error in the measurements was associated with the main limitation of the method being considered, viz., a decrease of the electrolyte volume as samples are taken for analysis. This limitation could not be eliminated by decreasing the sample volumes since working with very small samples reduces the sensitivity of the measurements.

The complications described above could be eliminated, if, instead of taking electrolyte samples at regular intervals, the whole electrolyte volume in which dissolution occurs were replaced from time to time. But such replacement is expedient only if the interruption of the electrochemical process does not affect the dissolution rate of the electrode, the dissolution process occurs relatively slowly (≥ 60 min), and complete electrolyte removal from the cell can be easily ensured. This practice was justified by the experimental data obtained in the investigation of the dissolution processes of solid electrodes made from corrosion-resistant metals.⁽¹³⁷⁾ Figure 24 shows a simple set-up for investigation of such processes.

An improved method that can be used for liquid (amalgams) and solid (metals and alloys) electrodes in the investigation of fast and slow dissolution processes is based on dispensing out a part of the electrolyte, in order to measure its radioactivity, from the working cell into a special measuring cell located near the radioactivity counter and shielded with lead against radiation

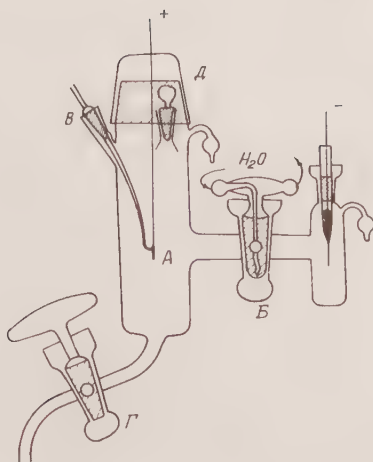


Figure 24. Design of the measuring cell: (A) working electrode, (B) cooled stopcock for separation of the anode and cathode chambers, (B) bridge for potential measurement, (Г) tap for solution discharge, (D) tap for solution supply.⁽¹³⁷⁾

from the electrode. The main features of this method and the sequence of measurements coincide with those of the "solution" method for adsorption measurements on electrodes described above (see Section 2). A version of this method as applied to the dissolution processes of amalgams was developed by Losev.^(123,124) The schematic of the set-up proposed by him is shown in Figure 25. In this set-up circular vessels mounted on a cylindrical Geiger counter or flat cylindrical glass vessels with thin walls (0.1 mm thick) are used as measuring cells. This method is free of the main drawbacks of the "sampling" method. The measurements are performed without disturbing the hermetic sealing of the set-up, without interrupting the dissolution process, and without loss of electrolyte, because after the radioactivity measurement the sample is returned to the main cell. A major portion of the electrolyte can be sampled

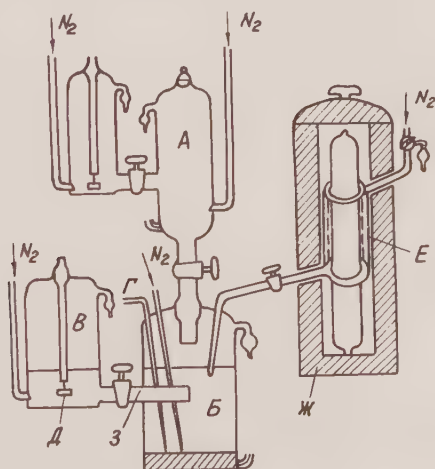


Figure 25. Schematic of the set-up: (A) vessel for preparation of labeled amalgam, (B) main cell, (B) vessel for the auxiliary electrode, (Г) bridge for potential measurement, (E) measuring cell, (Ж) lead shield, (3) tube.⁽¹²⁴⁾

for radioactivity measurement. This enhances the accuracy and sensitivity of measurements, which are now limited only by the sensitivity of the radiometric equipment and the specific radioactivity of the labeled preparations. This version of the method allows the dissolution rate to be measured as a function of potential, temperature, solvent nature, and solution and amalgam composition. Its advantage is that γ and hard β isotopes can be used as a label for the metal undergoing dissolution and it is possible to work with soft β isotopes ($E_\beta \leq 0.4$ meV) if the walls of the measuring cell are made from inert, thin polymeric material (5–10 μ K thick). The method can be as successfully used for solid electrodes.

It has been shown^(123,124) that with the version of the method under consideration the rate of the ionization process of the metal in an amalgam can be measured both under anodic and cathodic polarizations of the amalgam. Hence it follows that the rate of ionization of the metal in the amalgam can be measured when it is much less than the rate of the reverse process—the discharge of metal ions.

Under these conditions, the current flowing in the solution-labeled amalgam system is equal to the difference of the true rates of the cathodic and anodic processes at a given potential

$$i = i_K = i_a$$

If at time t the radioactivity of the solution is I and the amalgam radioactivity is $(I_0 - I)$ (I_0 is the initial radioactivity of the amalgam before contact with the solution), the increase in the solution radioactivity (dI) in the time dt is:

$$dI = \frac{(I_0 - I)i_a S dt}{m_a n F + (i_K + i_a) S t} - \frac{I i_K S dt}{m_p n F - (i_K - i_a) S t} \quad (14)$$

where m_a is the number of g-moles of labeled metal in the amalgam; m_p is the number of g-moles of the salt of this metal in solution; S is the amalgam surface; n , F are constants; and I is the solution radioactivity at time t .

In the course of the experiment, the amalgam and solution concentrations change. But if the initial concentrations as well as the volumes of these phases are large, the change of m_a and m_p during the experiment may be neglected. Then the previous equation reduces to

$$dI = \frac{i_a S I_0}{m_a n F} \left[1 - \left(1 + \frac{m_a i_K}{m_p i_a} \right) \cdot \frac{I}{I_0} \right] dt \quad (15)$$

After integration of this equation at $I = 0$ and $t = 0$, we have the equation

$$\ln \left[1 - \left(1 + \frac{m_a i_K}{m_p i_a} \right) \cdot \frac{I}{I_0} \right] = - \frac{i_a S}{m_a n F} \left(1 + \frac{m_a i_K}{m_p i_a} \right) \cdot t \quad (16)$$

which after some mathematical transformations can be significantly simplified if I is several orders smaller than I_0 . In this case the expression for the

dependence of the radioactivity value of the solution on time is given by

$$I = \frac{i_a I_0 S}{m_a n F} \cdot t \quad (17)$$

From this equation the true rate of the anodic process i_a can be calculated if the coefficient of the slope of the straight line expressing the dependence of I on t is known. A quantitative processing of the experimental data obtained under such conditions is possible only if the radioactivity of the electrolyte solution is lower than that of the amalgam by several orders of magnitude. The use of amalgams with high radioactivities leads to a considerable increase of the background near the measuring cell, so that the measurement of the solution samples with low radioactivities becomes unreliable. In other words, there arise some difficulties in the measurement of the initial stages of the dissolution processes in the case of cathodic polarization. The investigation of the dissolution rate of metal in the presence of cathodic polarization is further complicated in the case of a solid metal electrode by the slowness of the diffusion of the isotope in the solid phase. For this reason, the experimental data obtained for such processes on solid electrodes⁽¹⁵²⁾ require verification.

The method under consideration is generally not used for determination of the rate of the cathodic process—the discharge of metal ions—because in this case the rate is determined from the decrease in the radioactivity of the solution and the error in the measurement of this decrease is very large, as follows from the analysis of the limitations of the “solution” method of adsorption measurement.

As applied to the dissolution process, the disadvantages of the method proposed in References (123) and (124) are as follows. Only comparatively slow dissolution processes can be studied since sampling, measurement of the samples, and their return to the main cell takes some time, and a reliable determination of the curve of radioactivity increase with time necessitates taking 4–5 samples. Moreover, in the case of fast electrode processes the errors resulting from inaccurate determination of the moment of time to which a particular sample corresponds (the “lag” effect) increase since the dissolution process is continuous.

In references^(130,131) a new design of a set-up for investigation of the dissolution processes of amalgams was proposed which involves solution circulation through an auxiliary side tube. A schematic diagram of such a set-up is shown in Figure 26. The main feature of the design of this set-up is an exactly centered magnetic stirrer by means of which amalgam and solution are stirred and the solution circulation through a side tube is ensured. The side tube serves for continuous withdrawal of solution from the main cell to measure its radioactivity. The advantage of this set-up is that in it the “lag” effect is less. This makes it possible to study quantitatively fast electrode processes (the time required for uniform distribution of electrolyte in the main cell is 3–4 s) and to record automatically the fast increase of the solution

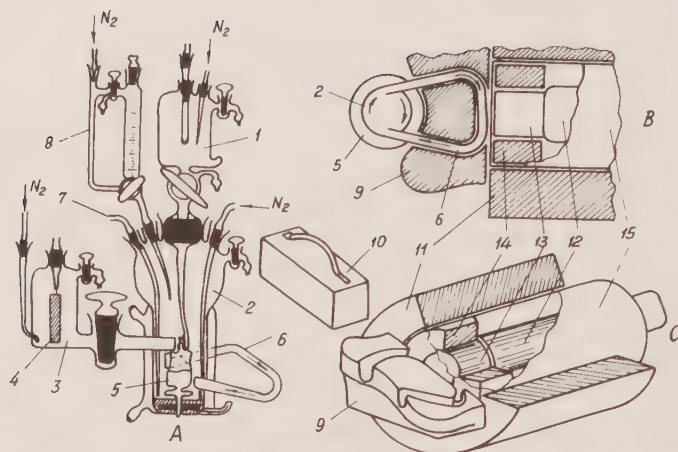


Figure 26. Schematic of the set-up: (A) glass cell, (C) protection chamber with the scintillation counter, (B) top view of the bottom part of the central cell and of the protection chamber, (1) upper cell, (2) central cell, (3) cell for auxiliary electrode, (4) auxiliary electrode, (5) stirrer, (6) circulation tube, (7) electrolytic gate, (8) burette, (9), (14) protection shields, (10) bushing, (11) "house", (12) photomultiplier, (13) scintillator, (15) sensor.⁽¹³⁰⁾

radioactivity. The latter aspect imposes great requirements on the radiometric equipment. In view of the wide range of the change in the solution radioactivity, the radiation counters must have a high resolving power. In addition, due to the small amounts of the solution present at a time in the side tube, counters with a high radiation registration efficiency are required. The fast change in the solution radioactivity and the necessity for its continuous registration define the characteristics of the scaling units, primarily their fast response. It has been shown^(130,131) that counters based on scintillation crystals meet practically all these requirements. For investigation of fast dissolution processes of solid electrodes, it has been suggested⁽¹³¹⁾ that a layer of test metal labeled with a radioisotope be applied to the platinum blades of a magnetic stirrer. Then by means of the set-up shown in Figure 26 it is possible in principle to measure the dissolution rate of a solid electrode. The chief drawback of this technique is the difficulty of applying labeled metal to the stirrer blades. This problem was covered in more detail above. Moreover, the necessity to use platinum as a material for the stirrer limits further the applicability of this technique.

The dissolution processes of solid electrodes labeled with radioisotopes of soft β -radioaction can be successfully studied by means of a cell with the bottom or walls made from a thin polymeric material, just as for investigation of the adsorption from solutions on solid electrodes (see Section 2). In this case the dissolution process is studied by continuous measurement of the solution radioactivity through a membrane serving as the bottom of the electrochemical cell. The radioactivity counter is located directly over the

membrane. The stirring of the solution is effected by inert gas. The main advantages of this cell consist of the following.

It is possible to do without a special measuring cell shielded with lead against radiation from the electrode and to register the solution radioactivity directly in the main cell, protecting the counter from radiation from the electrode by a solution layer. This greatly simplifies the design of the set-up and decreases the "lag" effect in the registration of the change of the solution radioactivity. With effective stirring, the "lag" effect is practically completely eliminated, which, in conjunction with automatic registration of the solution radioactivity, makes the technique applicable to fast dissolution processes.

When a radioisotope is introduced into the specimen by irradiation in a nuclear reactor, the radioactive tracer methods proposed in References (124), (130) and (131) are not applicable since, for the reasons pointed out above (the presence of micro-impurities, the necessity of preparation of samples before analysis, the length of the analysis), the return of the solution samples to the main cell after the radioactivity measurement is difficult and even undesirable. In this case it is advisable for dissolution studies to use a flowing-type cell. The design of such a cell, as proposed in Reference (139), is shown in Figure 27. With this design the solution is fed into the cell continuously by

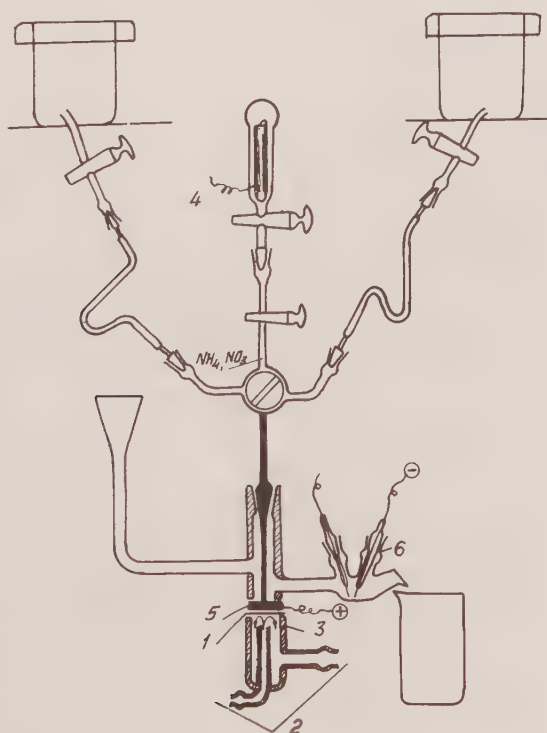


Figure 27. Schematic of a flowing-type cell: (1) thermocouple hole, (2) connecting tubes for connecting the thermostat, (3) copper gasket, (4) reference electrode, (5) working electrode, (6) auxiliary electrodes.⁽¹³⁹⁾

way of the reference electrode, which ensures the supply of fresh electrolyte portions to the electrode surface and allows the working volume of the cell to be reduced to 6–10 ml. The solution flows through the vessel in which an auxiliary electrode is located and is discharged into a receptacle. The rate of flow of the solution is kept constant and controlled by the height of the liquid level in the supply tank and the internal diameter of the feed tubes. The solution receptacle is changed from time to time and its content is analyzed by means of a gamma-spectrometer.

The chief advantage of the flowing-type cell is that it eliminates all the complications associated with introduction of the isotope into the specimen.

An improved version of the flowing-type cell allowing for work both with the electrolyte flow and for sampling at regular intervals with the electrodes immersed in solution and without breaking of the polarization current has been suggested⁽¹⁴⁰⁾ (Figure 28).

A common limitation of the flowing-type cells is a possible deposition of the dissolving metal on auxiliary electrodes, which reduces the accuracy of the obtained experimental data. At present there are no methods available to eliminate this limitation.

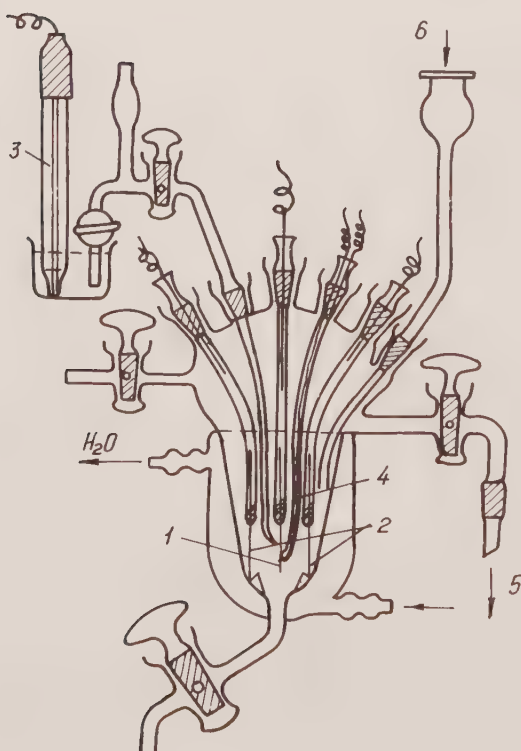


Figure 28. Schematic of a flowing-type cell: (1) working electrode, (2) auxiliary electrodes, (3) reference electrode, (4) thermocouple for measuring temperature, (5) solution discharges, (6) charging of solution.⁽¹⁴⁰⁾

3.2. Methods Based on the Determination of the Radioisotope Amount on the Electrode

The methods of this group are essentially as follows. A radioisotope is introduced into the specimen electrode by one of the methods described above, and then the electrode is subjected to electrochemical treatment in the course of which it undergoes dissolution. The dissolution rate of the electrode is determined by measuring, at regular intervals or continuously, the amount of the radioisotope on the electrode using radiometric or spectrometric equipment. With this method of registration of the dissolution rate, the "lag" effects are absent and good solubility of the corrosion products is not strictly necessary.

The common limitation of the methods of this group is that the change in the electrode radioactivity has to be registered in the presence of a large radioactive background, which results from the considerable amount of the radioisotope label initially introduced into the specimen. This means that the dissolution rate of the electrode can be reliably measured only if the change of the electrode radioactivity during its dissolution is more than 10% of the initial value. Now we shall discuss in detail the main features of the methods of this group.

For investigation of the dissolution processes of amalgams by measuring their radioactivity a method developed by Losev^(123,124) is sometimes used. The schematic of the set-up proposed by him is shown in Figure 29. The technique is as follows. For measuring the radioactivity of an amalgam during its dissolution, small samples (0.2 ml) are taken from it at regular intervals into a capillary (ϕ 1.0 mm in diameter) passed through the walls of a lead protection chamber, inside which a radioactivity counter is located. Due to strong absorption of radiation in mercury and in the capillary walls, the sensitivity of this technique is not high. In addition, it has all the shortcomings of the similar technique of dissolution rate measurement from radioactivity increase in solution described above. As shown by experimental data,⁽¹²⁴⁾ it is advisable to use this method only for investigation of amalgam formation processes, introducing the radioisotope label into solution. An improved version of this method has been suggested,⁽¹³¹⁾ in which the sensitivity is somewhat

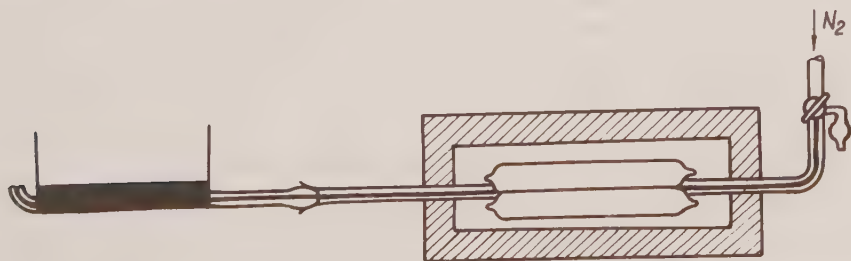


Figure 29. Bottom part of the cell for measuring true cathodic exchange currents (top part as in Figure 25).⁽¹²⁴⁾

higher and some of the shortcomings are absent. It is based on amalgam circulation through a side tube, as in the scheme shown in Figure 26.

In principle, the dissolution processes of solid electrodes can be studied by any of the radioactive tracer methods described above which are used for adsorption measurements (see Section 2). When used for investigation of the dissolution processes, the methods in question show the same advantages and disadvantages as in the adsorption studies. The general condition for the applicability of these methods to dissolution processes is that the entire amount of radioisotope present on the surface and in the electrode bulk should be measured simultaneously. This condition defines the specificity of each of the methods.

When using the method involving removal of the electrode into air for determination of its radioactivity (see Section 2), this condition of applicability is valid when working with thin electrodes in the case of β -radiators or in working with γ -radiators.

In the case of the techniques described in References (9), (57), (67), (80), (85) and (87), the condition of applicability holds true in working both with sufficiently thin electrolytic coatings and with hard β - and γ -radiators. In the latter case for the techniques described in References (9), (57), (67), (86) and (87), a regular or continuous replacement of the electrolyte portions in the cell is necessary in order to eliminate the influence of the solution radioactivity.

4. Methods Used for Investigation of Deposition Processes

Deposition processes have much in common with adsorption processes. For this reason, practically all radioactive tracer methods used for investigation of adsorption (see Section 2) are used to study deposition as well. However, due to the formation of fairly thick deposits during the deposition process, there arise some additional requirements.

The advantages and shortcomings of the methods described in Section 2 hold true in the case of their application to investigation of deposition processes. However, in the measurements by the "solution" method it is necessary also to take into account the influence of the change in the concentration of the substance being deposited on the deposition process itself, since, in accordance with the applicability criterion of the method, the concentration decrease should not be greater than 10%. For this reason, the "solution" method cannot be used for investigation of deposition processes from saturated solutions. In measurements by the "foil", "thin" layer, and "electrode lowering" methods, it is necessary to register the entire amount of radioactive substance deposited on the electrode; in the case of sufficiently thick deposits, radiation may be adsorbed inside the bulk of the electrode and this may lead to erroneous results.

So, the choice of isotopic label is complicated. In addition, in the case of the "foil" method, the fact that foil should be made from gold or platinum (see Section 2) reduces substantially the number of deposition processes to which this method can be applied.

The application of all the radioactive tracer methods mentioned above is possible only if the deposit does not crumble.

5. Use of Radioactive Tracers in Polarography (Radiopolarography)

Basically, the application of radioisotopes to polarography is as follows. The radioisotope present in solution is reduced to zero valence and forms an amalgam or an insoluble film with the mercury drop, which can be isolated from the solution and the radioactivity of which can be measured. The radioactivity value of each mercury drop will be constant at given potential and drop time. If the radioactivity of each drop taken separately is small, then the radioactivity of a known quantity of collected drops is measured. The drops are collected at known potentials. The radiopolarogram is obtained by plotting the radioactivity versus potential. The radioactivity of the collected mercury drops corresponds to the polarographic diffusion currents.

In working with radioisotopes, ordinary polarographic equipment is used. Before determining the radioactivity of a mercury drop, it is dried to increase the efficiency of recording of the radiation. The choice of the radiometric equipment to be used in this case depends on the kind of radiation emitted by the isotope label. By using spectrometers, it is possible to determine simultaneously several radioisotopes in the mercury drop.

The advantages of radiopolarography are as follows. It allows the formation of amalgams to be followed directly as a function of potential, time, and other parameters, and the influence on these processes of the solution composition to be determined. It can also be used to study the formation processes of complex amalgams.

If ordinary polarographic and radioisotopic measurements are used in conjunction, the possibilities of the polarographic method are materially increased, the reliability of the obtained experimental data is higher, and the sensitivity of the method is better.

Radiopolarography has been used for investigation of the formation processes of cobalt, zirconium, ruthenium, and thallium amalgams.⁽¹⁵³⁻¹⁵⁵⁾

6. Use of Tracers for Investigation of the Mechanism of Electrochemical Processes

As has been pointed out earlier in this chapter, the application of tracer methods to investigations of the mechanism of electrochemical processes is

based on the identity of chemical properties of different isotopes of an element. If an isotopic label is introduced into the test compound and the transition of this label into other compounds or phases during an electrochemical process is followed, then the mechanism of the transformation of the test compound in the course of the reaction can be determined. Both radioactive and stable isotopes can be used for this purpose, with their location during the course of the electrochemical process determined by radiometric and mass-spectrometric techniques, respectively.

The necessary conditions for the application of tracer methods to the investigation of the mechanism of electrochemical reactions are: first, the absence of an isotope exchange between the labeled substance and other compounds present in the system, e.g., solvent molecules; second, isotopic effects, which depend on the relative difference in the masses of the isotopes⁽¹⁵⁶⁾ and are particularly large for hydrogen isotopes, must be taken into account; third, the absence of radiation effects described above (see Section 3).

The tracer methods have been used most widely for investigation of the mechanism of the following electrochemical processes: oxidation and reduction of organic compounds,⁽¹⁵⁷⁻¹⁶⁰⁾ especially their transformation in the range of high anodic potentials,⁽⁴⁶⁻⁴⁸⁾ hydrogen evolution processes,⁽¹⁶¹⁻¹⁶⁴⁾ elucidation of the role of chemisorbed oxygen, anions, and surface oxides in anodic oxygen evolution processes,⁽¹⁶⁵⁻¹⁶⁸⁾ and formation of peroxide compounds.⁽¹⁶⁹⁻¹⁷²⁾

7. Conclusion

More than twenty years of experience in the use of tracer methods in electrochemical systems have shown that the relative simplicity of these methods and the ease of obtaining with their help a large amount of experimental data are to a large extent illusory. The application of tracer methods requires exceptional care and accuracy in experiments, and fulfillment of all necessary conditions. Primarily, attention should be centered on the possibility of the appearance of radiation-chemical effects and also on the radiochemical and chemical purity of isotopes. The importance of the latter factor can be illustrated by the history of the investigation of methanol adsorption on platinum by the tracer method.

The first data on the dependence of the extent of adsorption of methanol labeled with the isotope ^{14}C on the platinum electrode potential were obtained in 1967 by Smith and Urbach,⁽⁶⁶⁾ who found that this dependence has a maximum at 0.2 V and at this potential the extent of adsorption is 10^{-13} particles per cm^2 true surface. These data were at variance with the results obtained by electrochemical methods.⁽¹⁷³⁻¹⁷⁷⁾ In 1972 Sobkowski and Wieckowski⁽¹⁷⁸⁾ confirmed the previous isotopic tracer results⁽⁶⁶⁾ by a similar method. However, the reasons for the discrepancies between the data obtained by the tracer and electrochemical methods remained unexplained.

In 1975 Kazarinov *et al.*⁽¹⁰⁹⁾ proved that the reason for the differences in the experimental data was the presence of radioactive impurities in the labeled methanol preparations. It was suggested⁽¹⁰⁹⁾ that those impurities were the radiolysis products of methanol and a method of purification of labeled methanol preparations was proposed. Also, it was shown that the data on methanol adsorption on platinum obtained with purified methanol preparations coincide completely with those obtained by electrochemical methods.⁽¹⁷³⁻¹⁷⁷⁾

The above conclusions were confirmed by a later study,⁽¹⁷⁹⁾ in which the composition of methanol radiolysis products was roughly established.

The possibilities of most of the radioactive tracer methods considered above are now quite clear. Only fundamentally new techniques may offer new possibilities.

For a detailed review of the literature on the application of isotopes in electrochemical studies the reader is referred to Reference (180) where a fairly complete list of references (~300 references) is given.

Symbols

Γ	extent of adsorption (mol/cm ²)
I	radioactivity value (pulse/min)
C	concentration (mol/liter)
S	surface area (cm ²)
V	volume (ml)
β	counting efficiency of radiation
μ	radiation adsorption coefficient (cm ⁻¹)
E	electrode potential (V)
γ	roughness factor, equal to the true to visible surface ratio
θ	coverage of adsorbent surface
m	mass (mg)
F	Faraday number
i	current (A)
t	time (s, min)

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